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THE EXPLOSION HAZARDS OF AMMONIUM NITRATE AND AMMONIUM NITRATE BASED FERTILIZER COMPOSITIONS

A SUMMARY

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The Canadian Fertilizer Institute
and Contributing Bodies

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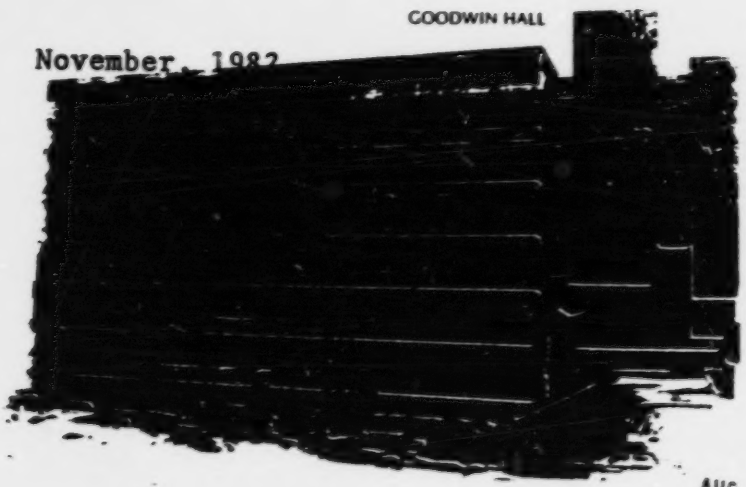

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- A SUMMARY -

A REPORT PREPARED FOR THE CANADIAN FERTILIZER INSTITUTE AND CONTRIBUTING BODIES BY THE

DEPARTMENT OF MINING ENGINEERING
QUEEN'S UNIVERSITY
KINGSTON, ONTARIO

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ABSTRACT

This report summarizes all of the work conducted at Queen's University over the life of the five year contract funded by the Canadian Fertilizer Institute and contributing bodies.

On the basis of the results from the research program, it can be stated that the shock sensitivity hazards presented by the molten material are significant, especially at elevated temperatures i.e. 260°C.

Since the molten material is the prime mover in any fire-to-explosion sequence, it is necessary that the shock sensitivity be quantified not only from the point of view of critical boosters, but also from plane shocks induced by slow moving projectiles. This has been done for molten ammonium nitrate at temperatures up to 260°C, and represents a significant step towards understanding the fire-to-explosion behavior of solid and liquid ammonium nitrate.

SUMMARY

This report condenses the bulk of the research conducted over the five year period of the contract, concluding with significant findings relating to the shock initiation of molten ammonium nitrate from the point of view of sensitivity to deflagrating compositions, as well as unstable metallic amine salts such as Tetramino Cupric Nitrate.

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INTRODUCTION

Ammonium nitrate is manufactured, stored and transported in very large quantities in Canada and worldwide. It is the essential ingredient in a variety of products, some of which are intended for use as fertilizers and others as explosives. The potential for destruction to increasingly large centers of population by the accidental or intentional explosion of large quantities of ammonium nitrate stored or transported within these centers, has, like liquified natural gas, become a focal point for concern.

The European Economic Community was the first in recent years to move towards establishing a basis for determining which of those varieties of ammonium nitrate fertilizers currently manufactured and transported were unduly sensitive to shock. The Council of the European Communities, proposed to determine at the Community level the characteristics and properties distinguishing ammonium nitrate based fertilizer from products based on ammonium nitrate manufactured for use as an explosive. To this end a directive was drafted and submitted to the European Communities which contained among new regulations regarding coatings and fillings for ammonium nitrate fertilizers of high nitrogen content, a series of tests to determine porosity, pH, size analysis, chlorine content, combustible material content and a detonability test (1).

The restrictions on impurities such as carbon content, chlorine, sulphur, transition metals, physical properties such as sizing and chemical properties such as pH, nitric acid content, as laid out in Annex 11 of the proposed EEC directive, are in keeping with those limits laid out by IMCO and most governmental regulatory bodies.

Such restrictions generally reflect the appreciation for the deleterous effects such materials can have upon the safe stowage characteristics and thermal stability of ammonium nitrate. These limits proposed in the latest EEC directive in no way conflict with the standards currently maintained by the Canadian fertilizer industry as they relate to ammonium nitrate.

However, the proposed detonability test as outlined in the EEC directive, chooses to place the whole issue of hazard analysis on the basis of a shock test designed around and for the solid material. Indeed, a quick review of the regulations regarding ammonium nitrate reveals that the bulk of the research upon which these regulations are based, deal directly with the solid material. The current approach to hazards presented by high ammonium nitrate based fertilizers or ammonium nitrate in general, ignores the fundamental hazard that has always been characteristic of ammonium nitrate, i.e. the great shock and heat sensitivity of the molten state, coupled with the unpredictable chemical reactivity when combined or contaminated with reducing agents.

Therefore, to classify or delineate those brands of ammonium nitrate fertiliser prills as either oxidizers or explosives on the proposed basis of a shock test is illogical, and has failed to come to grips with the real issue. That issue is to evaluate the nature of the hazard presented by ammonium nitrate under conditions of fire exposure, a situation which ultimately does not differentiate between ammonium nitrate types, their origin or proposed end use.

Any regulations dealing with the transportation, storage and handling of high ammonium nitrate based fertilizers must acknowledge the extreme explosion hazard presented by the molten material, especially at elevated temperatures, as well as the detonability of the original solid material.

It is obviously necessary to set a lower limit on the shock sensitivity of high nitrogen content fertilizers, for it is just as illogical to classify as an oxidizer, a material which can be detonated by a blasting cap. This must not be the only criterion.

The Oppau incident stands as testimony to the futility and false sense of security which can result from detonability tests used solely to evaluate whether or not a material should be classed as fertilizer (oxidant) or explosive. Indeed, the Oppau salt would not even be considered as a candidate for such a test (1).

EXPLOSION HAZARDS OF MOLTEN AMMONIUM NITRATE

Ultimately, the explosion hazards of ammonium nitrate under conditions of fire exposure center around the shock sensitivity of the molten material at elevated temperatures.

Current regulations dealing with the transportation, storage and handling of ammonium nitrate do not reflect this.

Upon detonation, ammonium nitrate yields an energy release of approximately 400 calories/gram. TNT, when detonated, yields an energy release of approximately 750-900 calories/gram. Thus, ammonium nitrate has roughly 50% of the strength of TNT when detonated completely.

By itself, this may not seem to be particulary significant until three factors are considered. First, ammonium nitrate in Canada alone, is currently manufactured to the extent of about 1,100,000 metric tons per year by the 8 major producers of both explosive grade and agricultural grade ammonium nitrate, and this quantity increases by about 5 to 8% per year (2).

Secondly, bulk storage piles for ammonium nitrate in Canada, which are typical of those currently used by the major producers, average 10,000 to 15,000 tons, and can go as high as 30,000 to 70,000 tons. It is not unusual to have a bulk storage pile measuring 200,000 to 800,000 cubic feet of bulk product in a near conical configuration, with a height of 15 to 25 feet. These large storage capacities are made necessary due to the cyclical requirements of the fertilizer industry (3).

Thirdly, the shock sensitivity of the molten material is much greater than that of the solid material, especially when high density prills are considered. Yet a complete detonation of a pool of molten ammonium nitrate containing 200 to 300 lbs. of material in contact with the bulk of the mass of solid prills, will almost surely initiate most if not all of the pile.

Consequently, the fate of the entire mass generally depends on what happens to the molten material.

When accidents with ammonium nitrate are reviewed, they can generally be classified as follows: a) boostering to explosion; b) fire to explosion; c) explosion without prior fire, and d) fires not leading to explosion. With few exceptions, all these accidents involved the liquid phase, either directly, or as an intermediate, whereby the explosion of the liquid phase initiated the solid, or semi-solid material.

Clearly, in spite of the large amount of research that has been done to date in investigating both thermal decomposition mechanisms and detonation characteristics of ammonium nitrate, very little is known about shock initiation mechanisms or detonation characteristics of the liquid phase material. Even more disturbing is the fact that this ignorance has tended to bias regulations regarding the transportation, storage and handling of ammonium nitrate towards the characteristics of the solid material, with little or no regard for the extreme shock sensitivity of the molten material, which is the prime mover in any explosion involving ammonium nitrate as the result of fire exposure. The complete detonation

of a 50,000 ton bulk storage pile with an energy release of approximately 50% of that of TNT is a possibility which has not been fully appreciated. This is partly due to: a) the lack of understanding of the magnitude of those shocks which are required to initiate molten ammonium nitrate, and b) the widespread belief that high density ammonium nitrate prills of the type used in agriculture (ρ_o - .85 grams/cm^3) can only be detonated with great difficulty, if at all.

Therefore, the explosion hazards of ammonium nitrate under fire exposure center around two factors: the shock sensitivity of the liquid phase material, especially at elevated temperatures; and the ability of large masses of solid ammonium nitrate to initiate and propagate a stable detonation.

The object of this five year study then, was to determine the shock initiation and detonation characteristics of molten ammonium nitrate as well as that of high density ammonium nitrate prills commonly used in agriculture, with a view to providing data useful in designing building codes for ammonium nitrate storage facilities, transportation and stowage containers, as well as fire fighting techniques.

INVESTIGATION OF THE SHOCK INITIATION AND DETONATION CHARACTERISTICS OF MOLTEN AMMONIUM NITRATE

A brief study of the minimum booster charge required for initiation of detonation in molten ammonium nitrate as a function of temperature was conducted by the U.S. Bureau of Mines in 1966 (4). The temperature ranges

studied varied from 180°C to 220°C. The results tended to indicate that at 220°C, molten ammonium nitrate is not unduly sensitive to shock, requiring about 50 grams of Tetryl to initiate it in 1.5 inch I.D. schedule 40 steel pipe, and 175 grams of Pentolite to initiate it in 4.6 inch I.D. glass vessels. At 180°C molten ammonium nitrate could not be initiated in 1.63 inch I.D. by .64 inch wall steel tubes with a 100 gram Tetryl booster, nor could it be detonated in large diameter glass containers (4.6 inch and 5.6 inch I.D.) using 170 to 570 gram Pentolite boosters.

More recently, an investigation conducted by the Technological Laboratory (TNO), in Rijswijk, Netherlands, in 1973, studied the detonation characteristics of molten ammonium nitrate and ammonium nitrate-water solutions over approximately the same temperature range and arrived at results in general agreement with that of the U.S. Bureau of Mines (5).

Both of these studies, however, failed to examine the molten material at much higher elevated temperatures. Furthermore, the tests were conducted without determining the density as a function of temperature; and the detonation velocity data was sketchy and incomplete.

Generally, these studies have been hampered by the facts that the studies must be conducted at temperatures of 180°C to 260°C. Molten ammonium nitrate is also an extremely corrosive fluid, comparable to that of nitric acid, and most work must be conducted in vessels of pyrex, stainless steel or aluminum. Further, molten ammonium nitrate is a very

powerful oxidizer, igniting some combustible materials with which it comes in contact, and reacting explosively with others. These factors make molten ammonium nitrate an extremely hazardous material to work with at elevated temperatures, especially on a large scale.

Studies involving the detonation stability of high density solid ammonium nitrate generally involve large masses (> 1 ton) and as such present formidable problems in locating sites suitable for such testing.

These are but a few of the reasons why studies involving these materials have either lagged or not been conducted at all.

The object of this research then, is to determine the shock initiation and detonation characteristics of both molten and solid ammonium nitrate, with emphasis on the molten material, as follows:

1) Determine idealized detonation state parameters for ammonium nitrate as a function of density from 0.5 to 1.5 grams/cm^3;
2) Establish an equation of state for molten ammonium nitrate at 190°C and extend the results to 260°C;
3) Conduct a series of card gap tests on molten ammonium nitrate over a temperature range of 220°C to 260°C, for the purpose of determining critical impact pressures necessary to establish a stable detonation in 5 inch diameter charges;
4) Determine the detonation characteristics of molten ammonium nitrate at elevated temperatures as follows:
   a) density determinations of the liquid phase system over a temperature range of 175°C to 260°C

b) critical primer weights and types necessary to initiate a stable detonation in the liquid phase system

c) critical diameter determinations on confined and unconfined systems

d) velocity of detonation studies as a function of temperature and diameter

e) sonic velocity determinations in the liquid phase system over a temperature range of 170°C to 260°C;

5) Evaluate the detonation characteristics of prilled ammonium nitrate, with emphasis on the high density material;

6) Evaluate the sensitivity to shock of molten ammonium nitrate and ammonium nitrate based fertilizer solutions to low amplitude - long duration shocks by means of projectile impact tests;

7) Evaluate the conditions under which molten AN may de initiated to a state of detonation by deflagrating-type compositions.

8) Cook-off tests with and without impurities.

1. DETONATION STATE PARAMETERS OF AMMONIUM NITRATE AS A FUNCTION OF DENSITY

Detonation state parameters include values such as gas volume (moles per hundred grams), heat of detonation (calories per gram), detonation pressure (kilobars), velocity of detonation (thousands of meters per second), particle velocity (thousands of meters per second), and detonation temperature.

Idealized detonation state parameters differ from experimentally determined values in that these values are determined from thermohydrodynamic theory and high temperature gas equilibrium calculations, and as such are completely free from the effects of charge confinement, particle sizing and charge diameter.

A comparison of these values with experimentally determined values indicates the extent to which the reaction of the explosive particles inside the detonation head is affected by external confinement, particle sizing, etc...

Initiation and propagation of detonations in liquid explosives are very complex phenomena. When initiation and propagation of reactive shocks become primarily functions of bulk density (hence charge temperature), a study of the changes in bulk density as a function of temperature also becomes important, as shown in Figure 1.

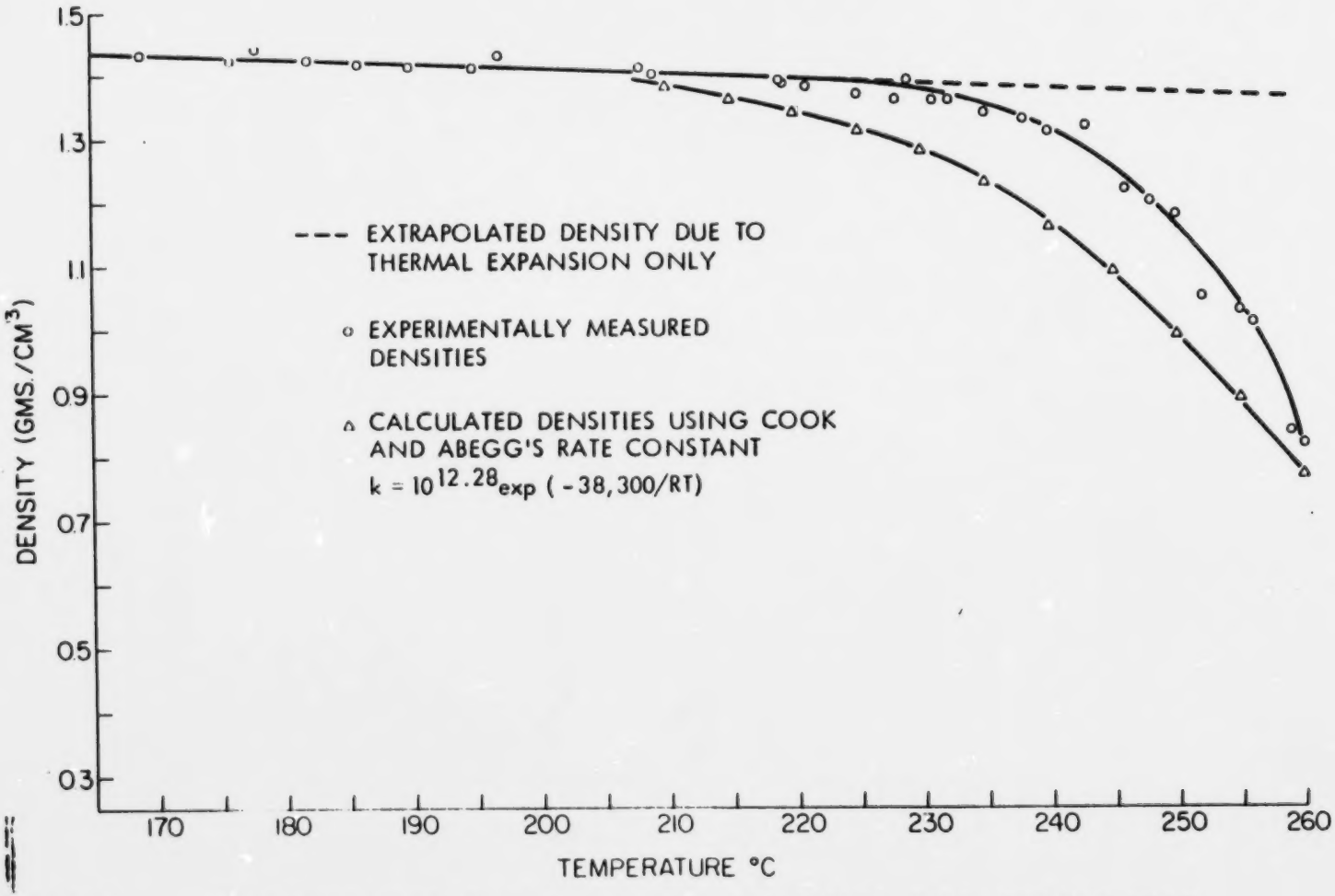


FIGURE 1 EXPERIMENTALLY DETERMINED DENSITIES AND CALCULATED DENSITIES FOR LIQUID PHASE AMMONIUM NITRATE FROM 170° C TO 260° C.

At temperatures much less than 220°C, chemically pure ammonium nitrate does not undergo sufficient "autoaeration" as a result of thermal decomposition to create enough bubbles for reaction sites or hot spots. These bubbles, when in sufficient numbers and of the correct size, collapse under the impact of the shock wave, and as a result of this adiabatic compression, become very hot and begin to burn from the inside out. For granular explosives the process is reversed.

Detonation state parameters and detonation state products were determined using CIL's "DTONATE" program, which uses the Cook equation of state as the basis for calculations. The bulk density of the ammonium nitrate was varied from 0.5 to 1.5 grams/cm^3 in .05 gram/cm^3 increments, and the detonation parameters and detonation state products are calculated accordingly. The data are then plotted as a function of density.

Chemical equilibrium at the Chapman-Jouguet plane was calculated by considering 34 possible reaction products.

In the case of ammonium nitrate, however, only six species are present in significant amounts, i.e. NO_2, NO, H_2O_2, H_2O, O_2 and N_2. Because of the method of calculation, a small amount of C was introduced.

RESULTS

Detonation parameters and reaction products were calculated for ammonium nitrate by use of CIL's "DTONATE" program over a density range of .5 to 1.5 grams/cm^3. The results are summarized in Figures 2 to 11

Figures 2 and 3 show the effect of density of concentrations of NO_2, NO and N_2 produced under detonation state conditions.

The concentration of NO remains essentially constant at .010 moles/100 gms until the bulk density reaches 1.3 gms/cm^3, at which point it begins to drop.

The concentration of NO_2 rises constantly with density. At a bulk density of approximately 1.0 gms/cm^3 the concentration of NO_2 rises steeply and at 1.4 gms/cm^3 the concentration in product gases exceeds that of N_2.

The concentration of O_2 behaves similarly to that of N_2, dropping off slowly at first until a bulk density of approximately 1.0 gms/cm^3 is reached, at which point the concentration of O_2 in the product gases drops off rapidly, as shown in Figure 4.

The concentration of H_2O behaves similarly to that of N_2 and O_2 in that it remains essentially constant until a bulk density of 1.0 gms/cm^3 is reached in the ammonium nitrate. At this point the concentration drops off rapidly. At a bulk density of 1.42 - 1.45 gms/cm^3

the concentration of H_2O_2 in the product gases does not exceed that of H_2O, as shown in Figure 5.

Figures 6 to 11 illustrate the behavior of detonation state parameters as a function of the bulk density of ammonium nitrate.

Both the gas volume and heat of detonation decrease with increasing density, as shown in Figures 6 and 7 respectively.

Detonation pressure, velocity and particle velocity increase with increasing density, in accordance with detonation theory, and this behavior is illustrated in Figures 8 to 10 respectively.

The detonation temperature increases to a maximum value at 1.3 gms/cm^3 and then rapidly drops off, as shown in Figure 11.

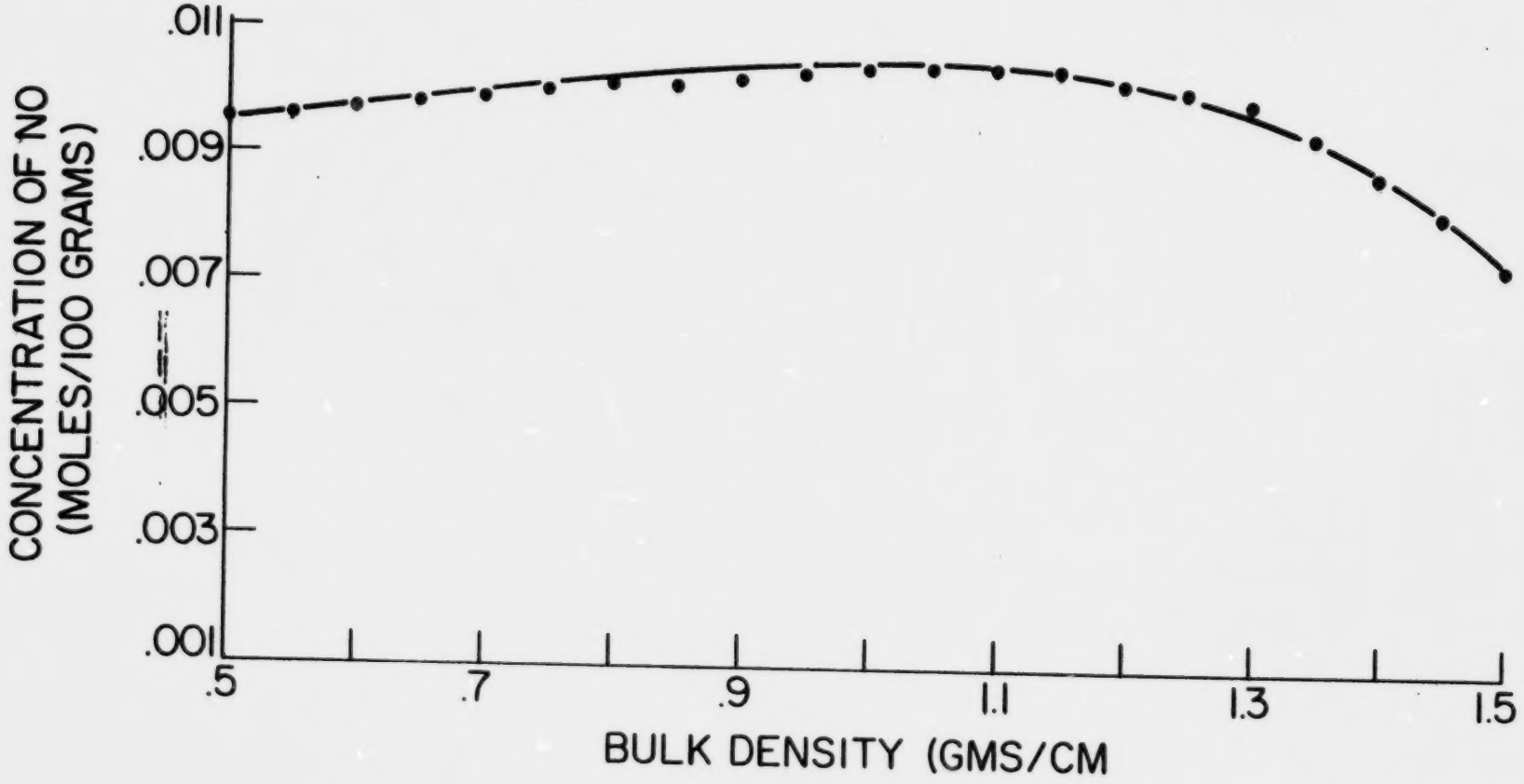


FIGURE 2 CONCENTRATION OF NITRIC OXIDE IN DETONATION PRODUCTS AS A FUNCTION OF DENSITY AS CALCULATED BY CIL's "DTONATE" PROGRAM.

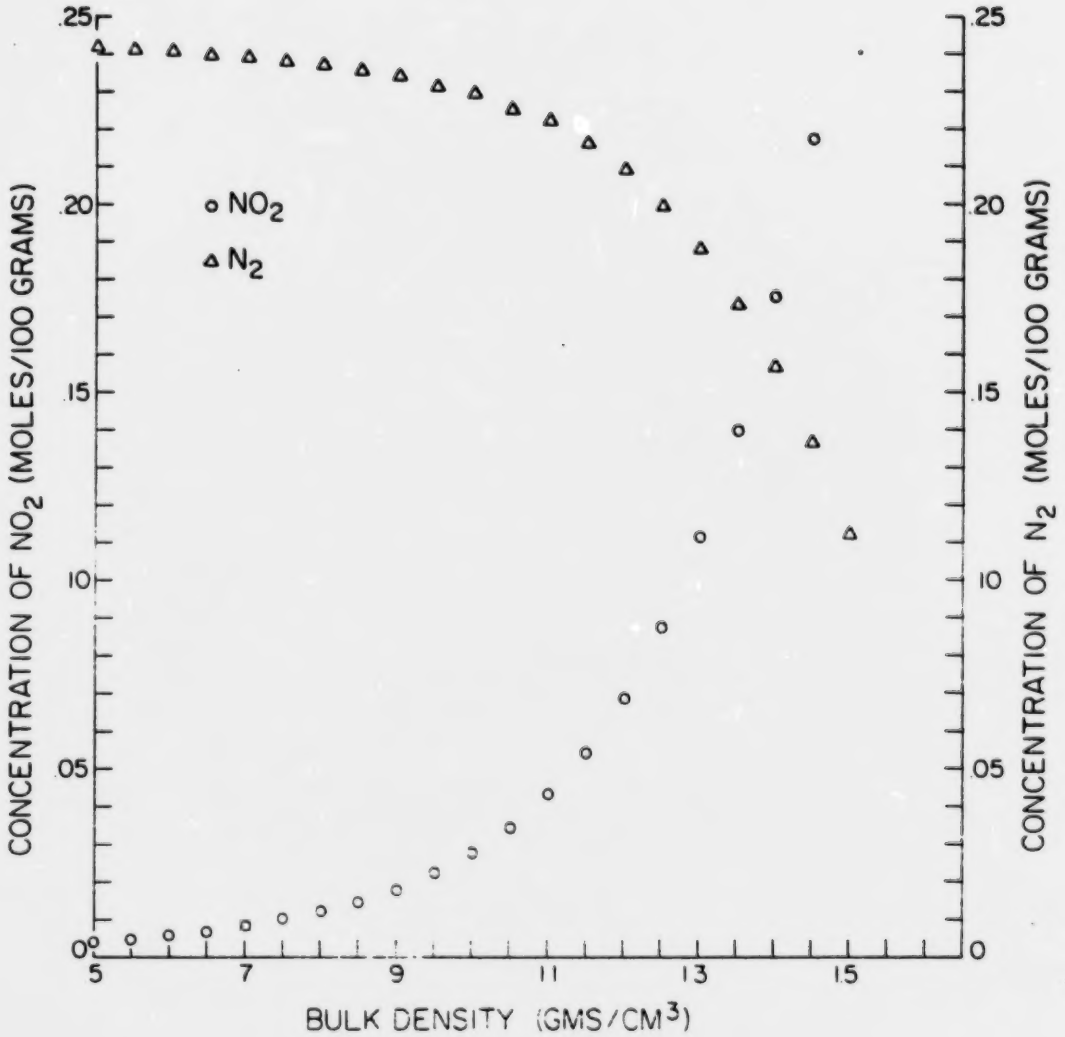


FIGURE 3 CONCENTRATION OF NITROGEN DIOXIDE AND NITROGEN ~~IN~~ DETONATION PRODUCTS AS A FUNCTION OF DENSITY AS CALCULATED BY CIL's "DTONATE" PROGRAM.

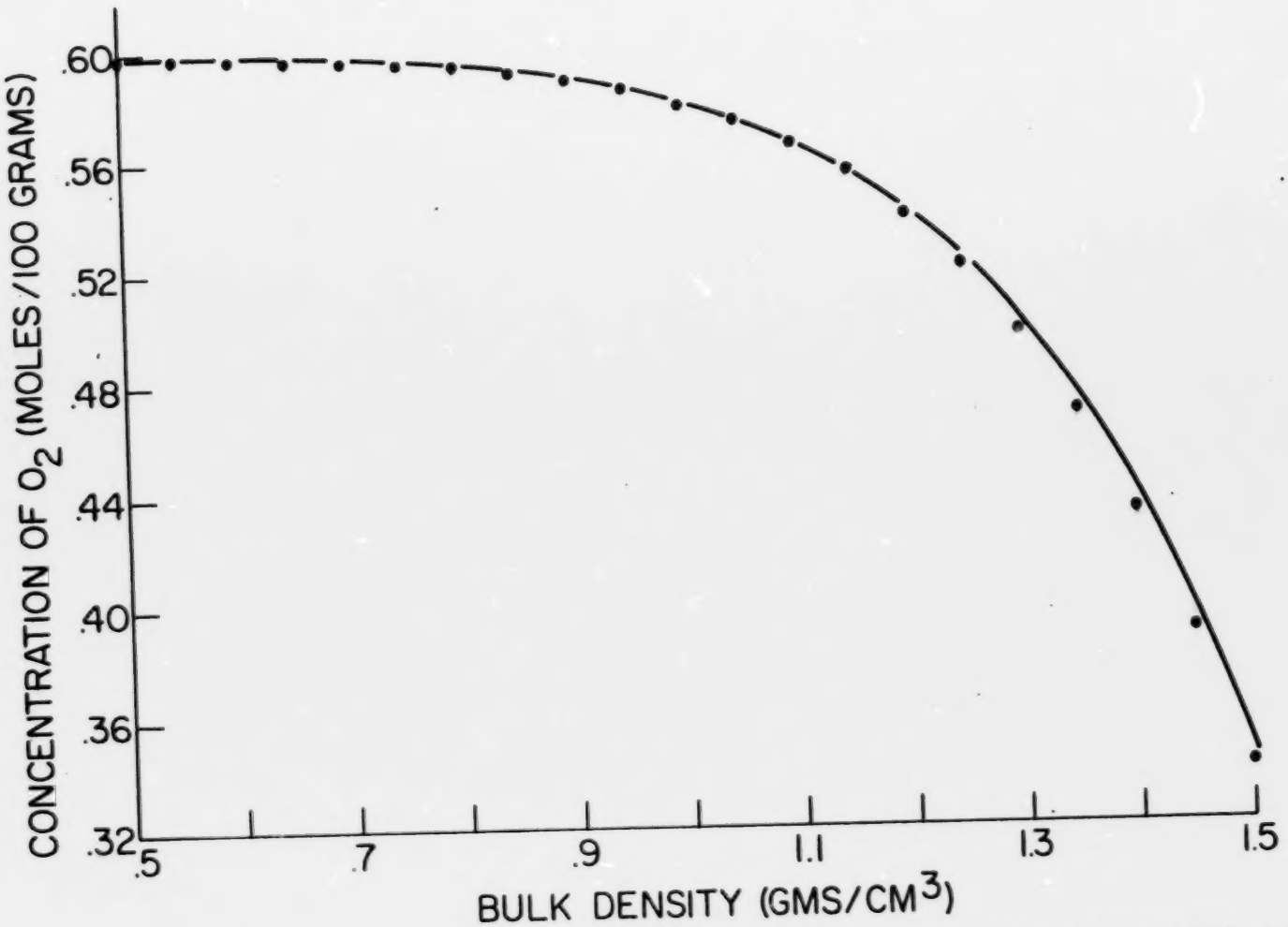


FIGURE 4 CONCENTRATION OF OXYGEN IN DETONATION PRODUCTS AS A FUNCTION OF DENSITY AS CALCULATED BY CIL's "DTONATE" PROGRAM.

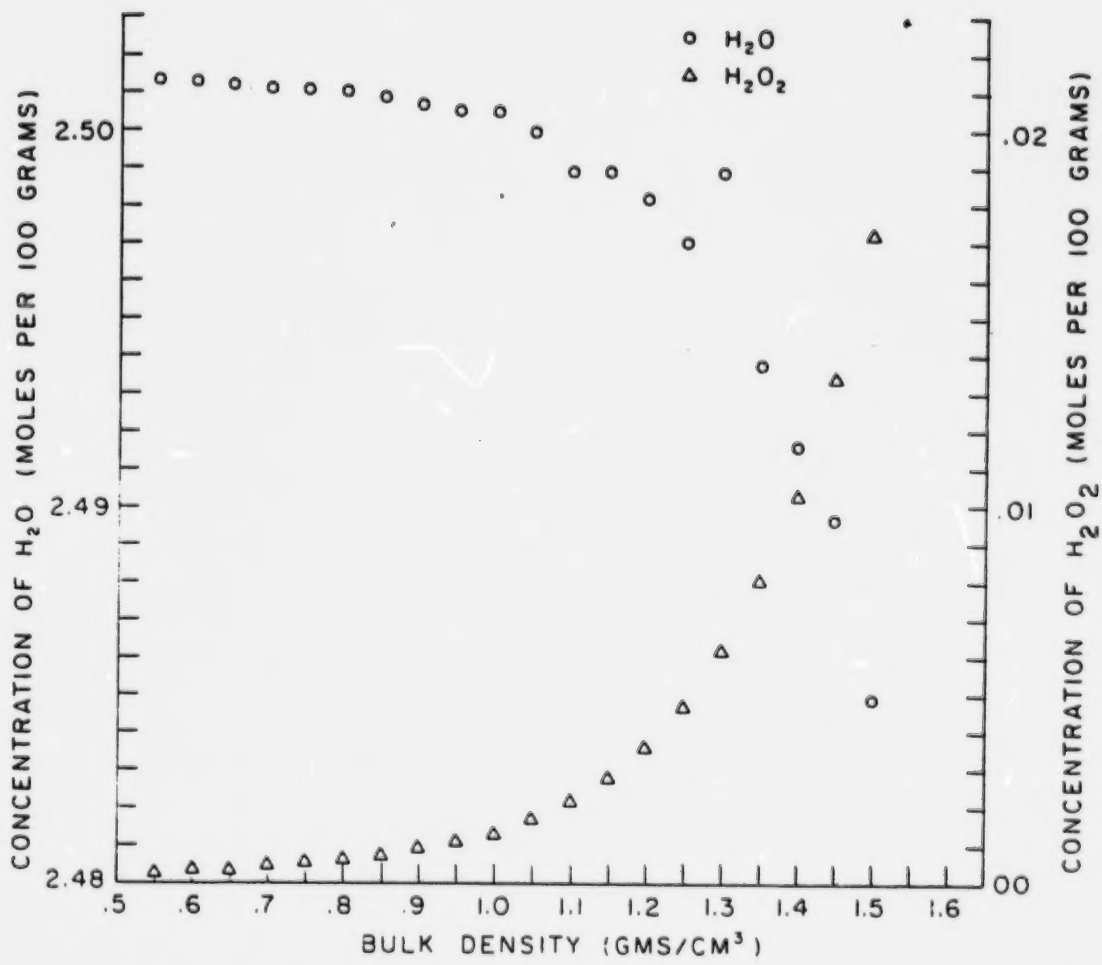


FIGURE 5 CONCENTRATION OF WATER AND HYDROGEN PEROXIDE IN DETONATION PRODUCTS AS A FUNCTION OF ~~DENSITY~~ AS CALCULATED BY CIL's "DTONATE" PROGRAM.

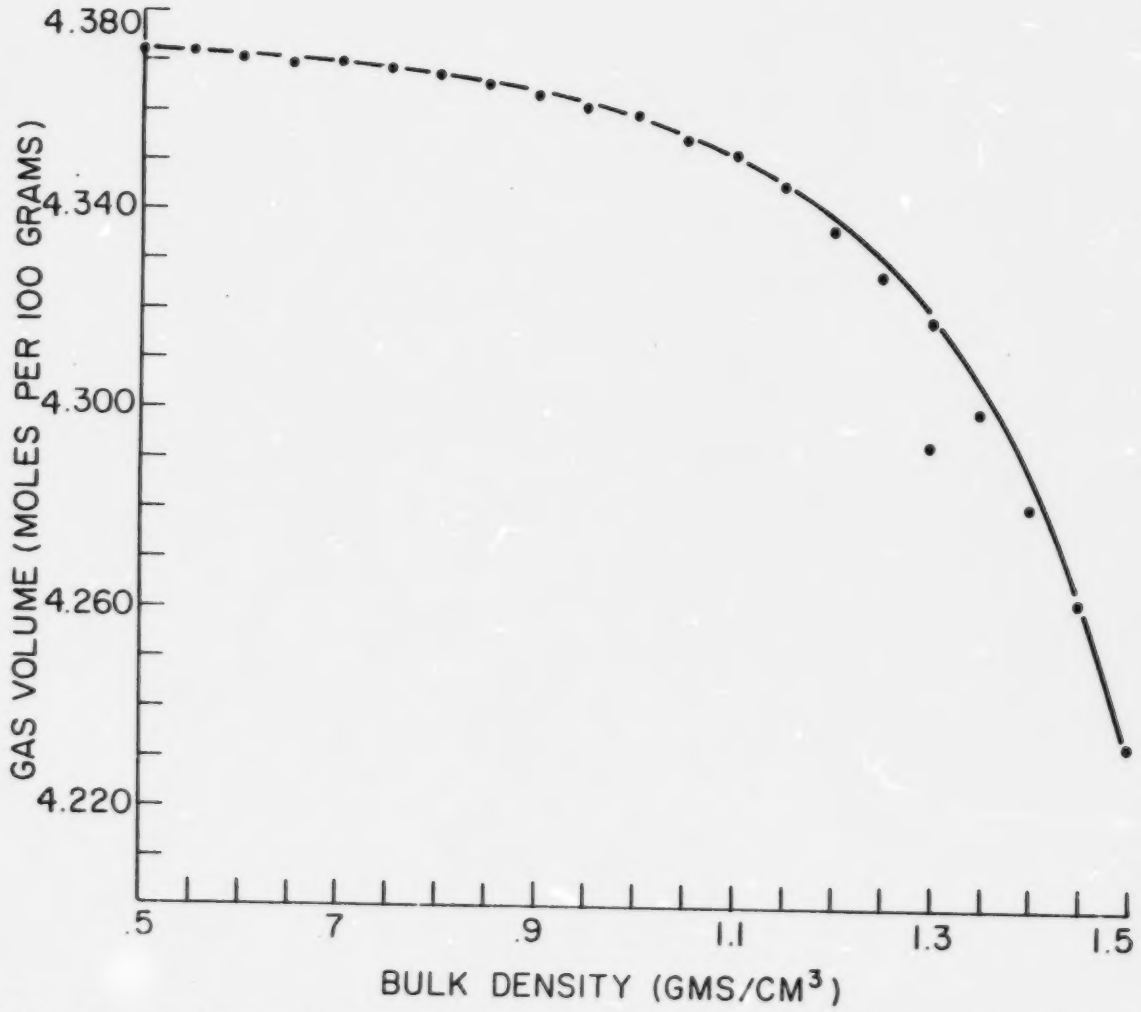


FIGURE 6 GAS VOLUME AS A FUNCTION OF DENSITY AS CALCULATED BY CIL's "DTONATE" PROGRAM FROM .5 TO 1.5 GRAMS/CM^3.

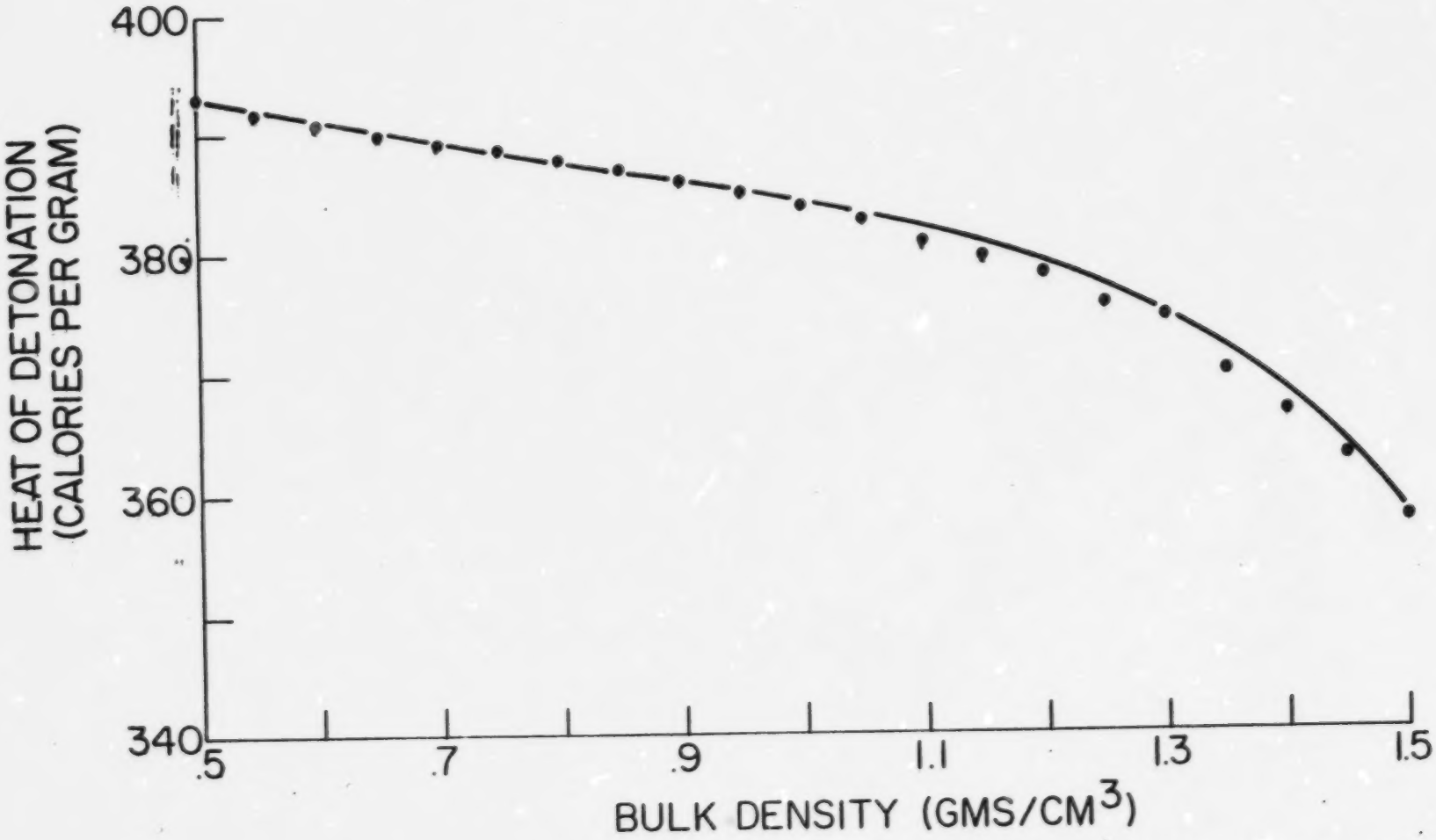


FIGURE 7 HEAT OF DETONATION AS A FUNCTION OF DENSITY AS CALCULATED BY CIL's "DTONATE" PROGRAM FROM .5 TO 1.5 GRAMS/CM^3.

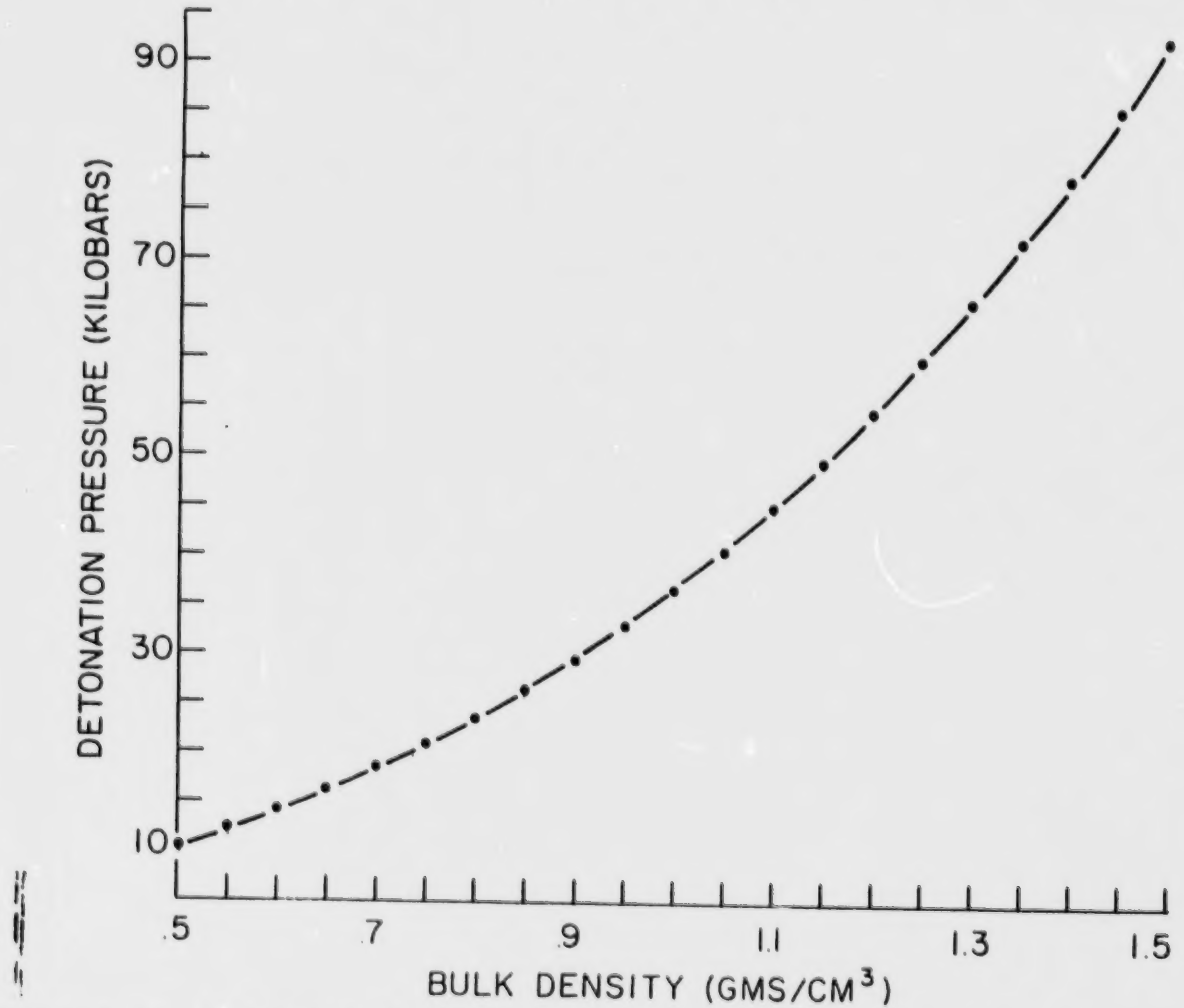


FIGURE 8 DETONATION PRESSURE AS A FUNCTION OF DENSITY AS CALCULATED BY CIL's "DTONATE" PROGRAM FROM .5 TO 1.5 GRAMS/CM^3.

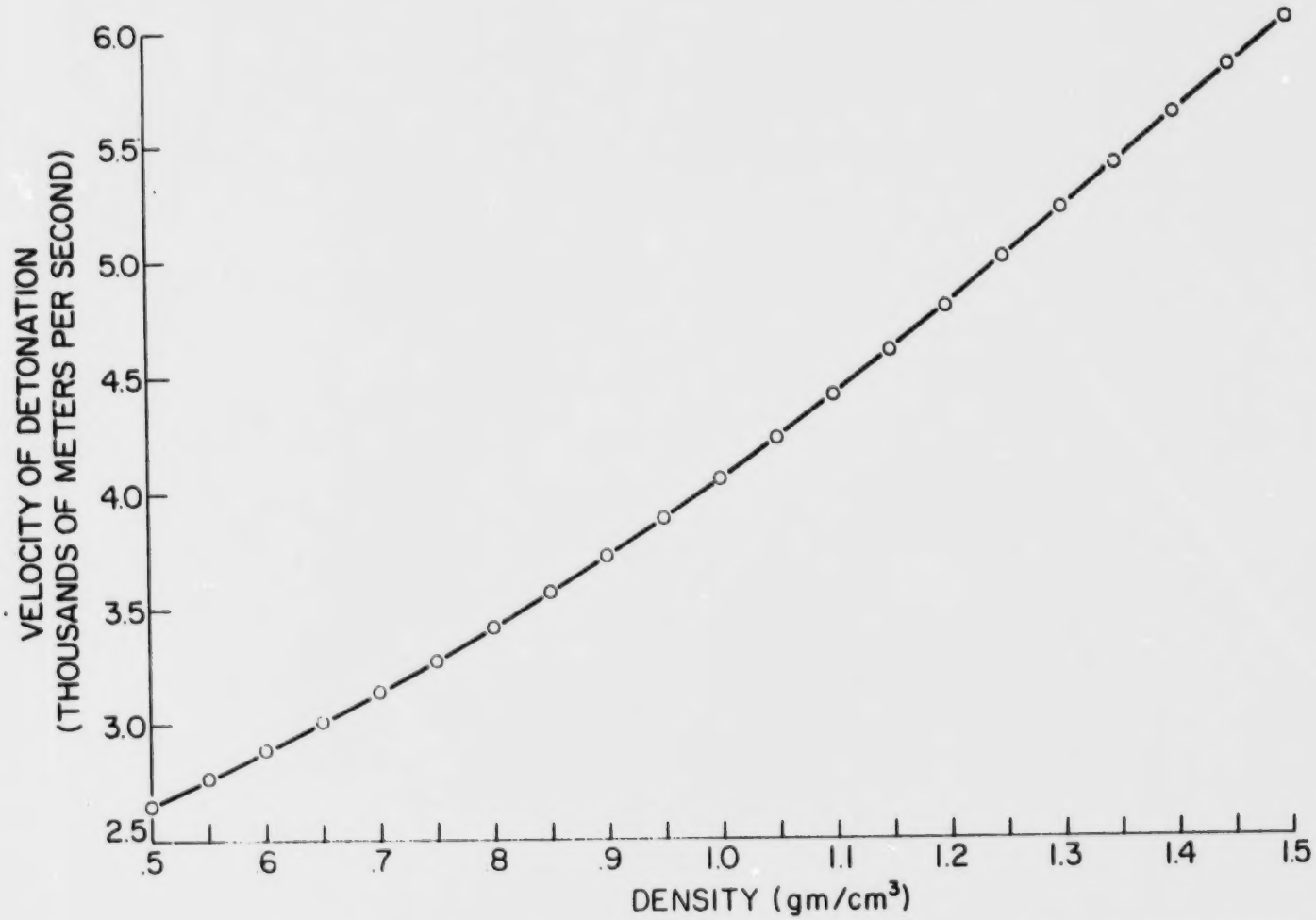


FIGURE 9 MAXIMUM THEORETICAL VELOCITY OF DETONATION OF AMMONIUM NITRATE AS A FUNCTION OF DENSITY FROM "DTONATE" EQUILIBRIUM PROGRAM AS COMPILED BY CIL, WHERE T_o=298°K.

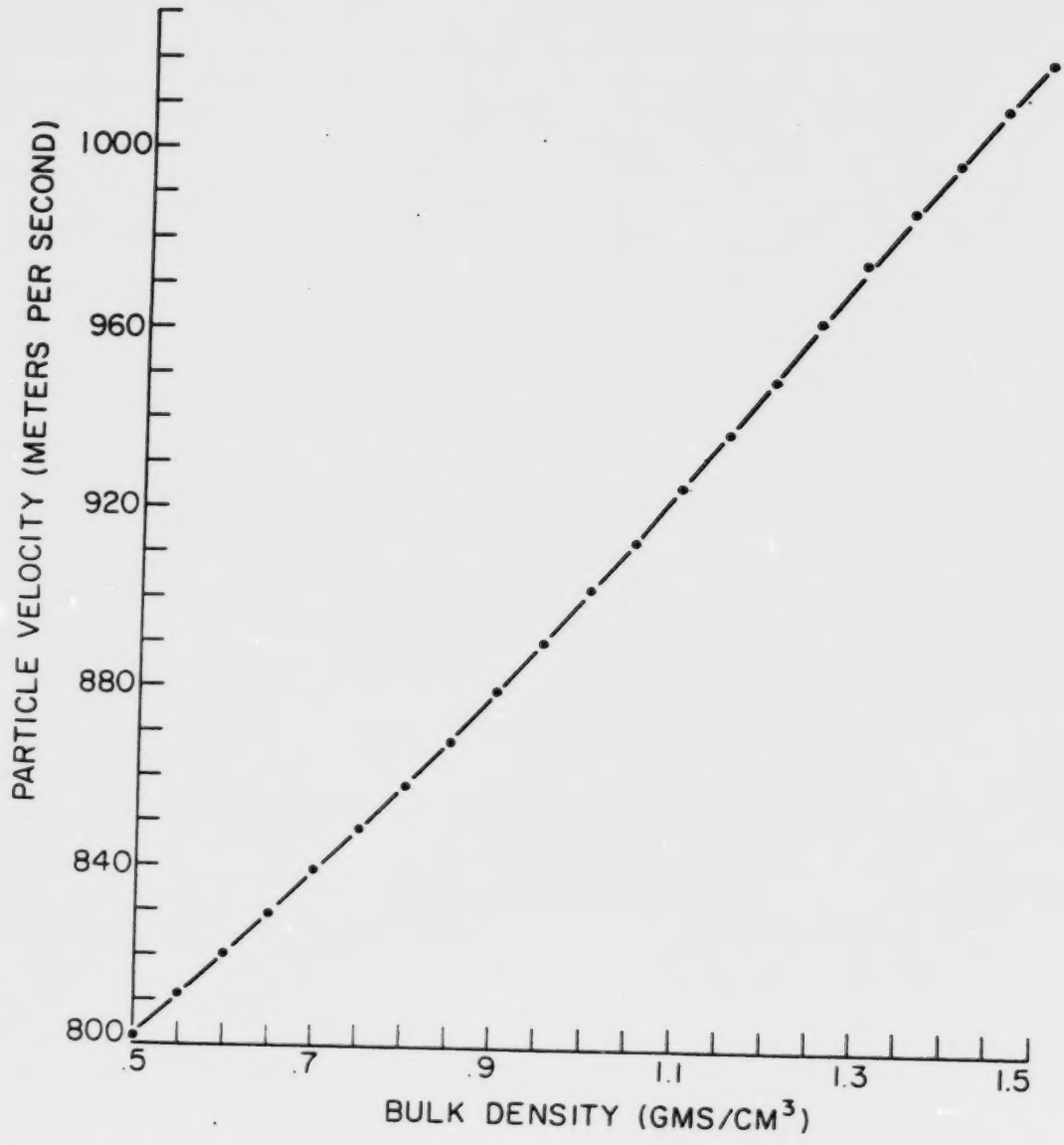


FIGURE 10 PARTICLE VELOCITY AS A FUNCTION OF DENSITY AS CALCULATED BY CIL'S "DIONATE" PROGRAM FROM .5 TO 1~~.5 GRAMS~~/CM^3.

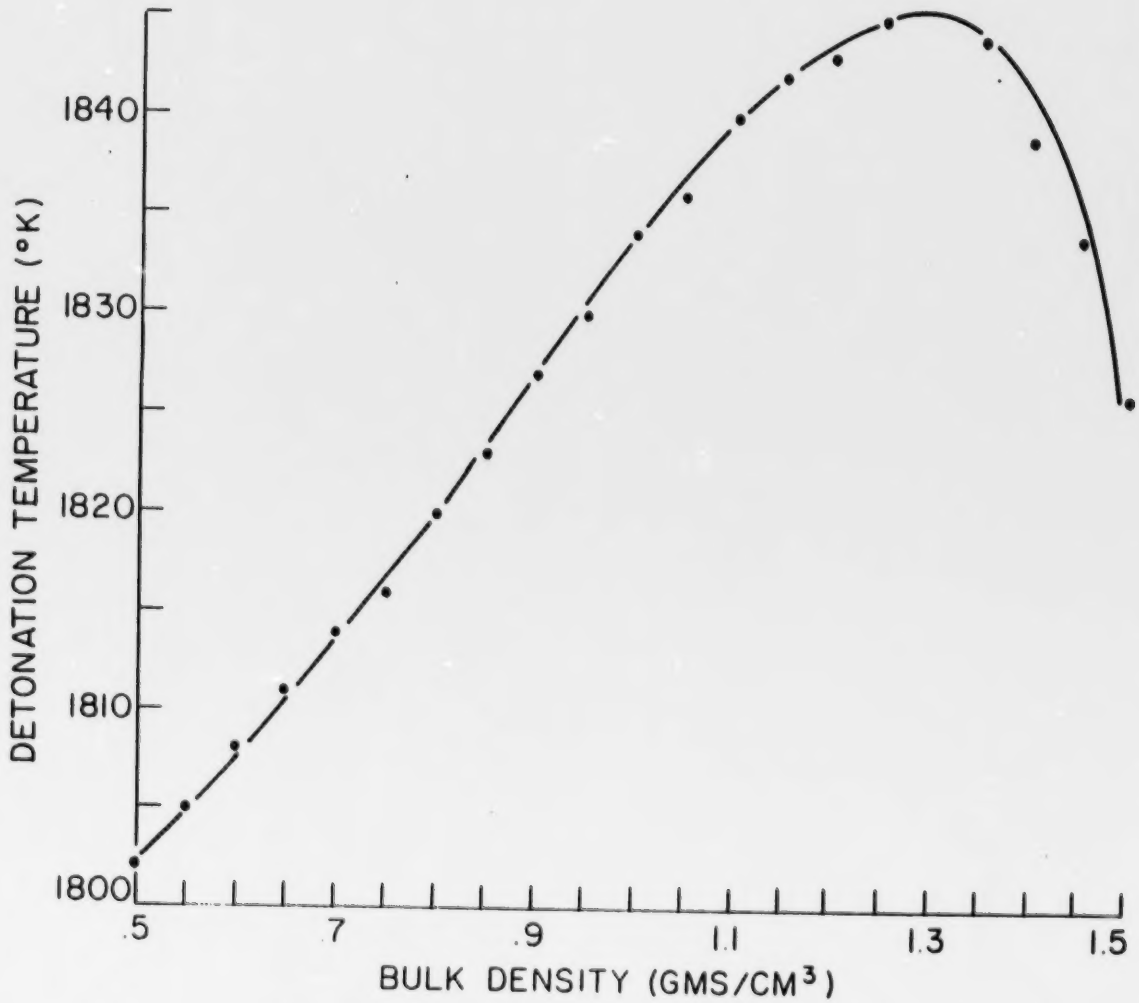


FIGURE 11 DETONATION TEMPERATURE AS A FUNCTION OF DENSITY AS CALCULATED BY CIL's "DTONATE" PROGRAM FROM .5 TO 1.5 GRAMS/CM^3.

CONCLUSION

The data presented herein would tend to indicate that, on the basis of theoretical calculations, ammonium nitrate at a density of ≈ 1.4 grams/cm^3 is quite an energetic material with detonation velocities (ideal) of ≈ 5500 m/s; a detonation pressure of ≈ 80 Kilobars; and a heat of detonation of ≈ 370 calories/gram.

TNT, for example, at a density of 1.56 grams/cm^3, upon detonation, yields ≈ 853 calories/gram (from theoretical calculations) and has a detonation velocity of ≈ 6835 m/s (ideal) at the same density.

This theoretical data would tend to indicate that ammonium nitrate, at a density of ≈ 1.4 grams/cm^3 will yield ≈ 43% of the energy in calories/gram that TNT would at a density of 1.56 grams/cm^3.

Also, the ideal velocity of detonation of ammonium nitrate at a density of ≈ 1.4 grams/cm^3 is ≈ 80% of that of the ideal detonation velocity of TNT at a density of 1.56 grams/cm^3.

Thus, ammonium nitrate, at high densities, is quite a powerful explosive when compared on the basis of theoretical calculations with other common explosives such as TNT.

Regarding the detonation products it would appear that the classic equation of a very energetic detonation of ammonium nitrate does not occur as written, i.e.

$$NH_4NO_3 \rightarrow N_2 + 2H_2O + 1/2O_2$$

Rather, the production of heavier molecules such as NO_2, NO and H_2O_2 appear to be the predominant mode for decomposition, with production of o_2, H_2O and N_2 dropping off with increasing density, while NO_2 and H_2O_2 concentrations increase rapidly with density.

2. THE SIGNIFICANCE OF EQUATION OF STATE DATA FOR MOLTEN AMMONIUM NITRATE

Determination of an equation of state for molten ammonium nitrate centers around determining the shock velocity and particle velocity in the medium at a temperature where, in the case of molten ammonium nitrate, the thermal decomposition rate is negligible. Small local discontinuities such as bubbles cause convergence of the shock wave and its associated mass flow, and can be a source of error in a typical experiment designed to determine the shock Hugoniot data of the unreacted explosive. Thus, all shock wave testing was done on the molten material at temperatures not greater than 190°C.

Voskoboinikov et al (6) have shown that the corresponding Hugoniot for a fluid containing bubbles can best be estimated by the equation

$$(1)\quad \left(\frac{Upa}{Up}\right)^2 = 1 + \frac{p}{Up^2} \cdot \frac{2}{\gamma + 1} \cdot \left(\frac{1}{\rho a} - \frac{1}{\rho}\right)$$

which relates the particle velocity of the "aerated" substance Upa, at the initial bulk density, a, to that of its condensed phase Up, for a given shock pressure where is the ratio of specific heats of gases and is the initial density.

This is quite significant for a material such as molten ammonium nitrate, where verification of the shock Hugoniot by optical means is difficult if not impossible at elevated temperatures.

Consider the familiar hydrodynamic relations

(2) $\frac{Upa}{Usa} = \left(1 - \frac{\rho ai}{\rho as}\right)$

and

(3) $Pa = \rho ai \cdot Usa \cdot Upa$

where Pa is the shock pressure in the "aerated" fluid; ρai is the initial density of the fluid before arrival of the shock wave, and ρas is the density of the shocked medium; Usa is the shock velocity in the "aerated" fluid, and Upa is the particle velocity of the "aerated" fluid. If the pressure vs particle velocity, or pressure vs shock velocity data for molten ammonium nitrate in a quiescent region can be determined, then by combining this data with Equation (1), all the other shock Hugoniots in the "aerated" state can be determined as a function of density, and hence temperature.

Indeed, little shock Hugoniot data are available for liquid explosives, because when shocked they usually readily undergo detonation. This behavior is, however, an important reason for obtaining such data. In the case of molten ammonium nitrate, quantitative measurements of shock initiation parameters, i.e. shock Hugoniot data, can be used to determine hazards from accidental shock initiation provided the amplitude of the donor shock wave can be determined.

Since the density has been shown to be a function of temperature for molten ammonium nitrate, it is to be expected that the shock sensitivity would also be affected by an elevation in temperature.

RESULTS

The experimental Hugoniot curve data for molten ammonium nitrate at 190°C ± 2C° and ρ_o = 1.42 gms/cm^3 is given in Table 1 below. The shock velocities are in kilometers/second, pressure in kilobars, V_o in cm^3/gm, where T_o = 190°C and P_o is equal to 1 atmosphere. The sonic velocity data point was experimentally derived.

From this data, a plot of shock pressure versus shock velocity and particle velocity was derived as shown in Figure 12.

The relationship between shock velocity and particle velocity is linear throughout the range of shock pressures tested, as illustrated in Figure 13. This is significant, since if the Hugoniot data of the unreacted explosive is being perturbed by chemical reaction of the explosive under shock loading at some point, an abrupt change in the slope of the line would occur. This did not occur, and the line intercepted the shock velocity axis very close to the velocity of sound in the explosive, at that density.

The Hugoniot curve for molten ammonium nitrate at 190°C at ρ_o = 1.42 is given in Figure 14.

In order to determine shock initiation thresholds and shock Hugoniots at elevated temperatures, i.e. at temperatures up to 260°C, it becomes necessary to calculate the necessary Hugoniot data for densities corresponding to this temperature range. This is due to the fact,

TABLE 1

Experimental Hugoniot Data for Molten Ammonium Nitrate at 190°C

T_o °C	V_o cm^3/gm	U_s m/s	U_{fs} m/s	U_p m/s	P_{KBARS}	V/V_o
190	.707	871	0	0	0	1
190	.707	2141	2608	1304	39.1	.391
190	.707	2498	3116	1558	54.4	.376
190	.707	2626	3344	1672	61.3	.363
190	.707	2634	3388	1694	62.3	.347
190	.707	2706	3558	1779	67.2	.342
190	.707	2800	3730	1865	72.9	.334
190	.707	2854	3858	1929	76.9	.324
190	.707	3244	4484	2242	101.6	.309
190	.707	3455	5026	2513	121.3	.272

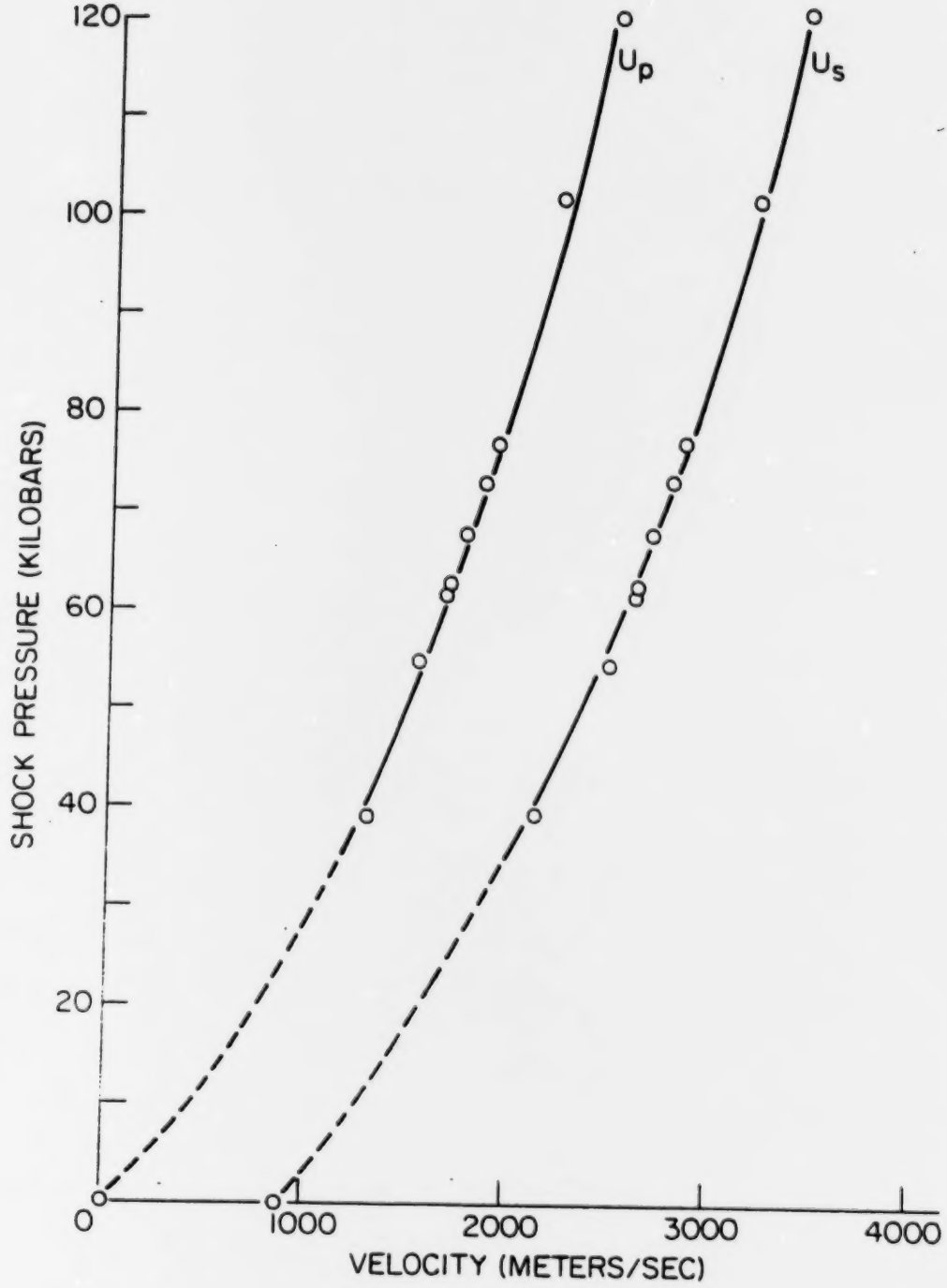


FIGURE 12 SHOCK ~~PRESSURE~~ IS SHOWN AS A FUNCTION OF PARTICLE VELOCITY AND SHOCK VELOCITY IN MOLTEN AMMONIUM NITRATE AT 190° C.

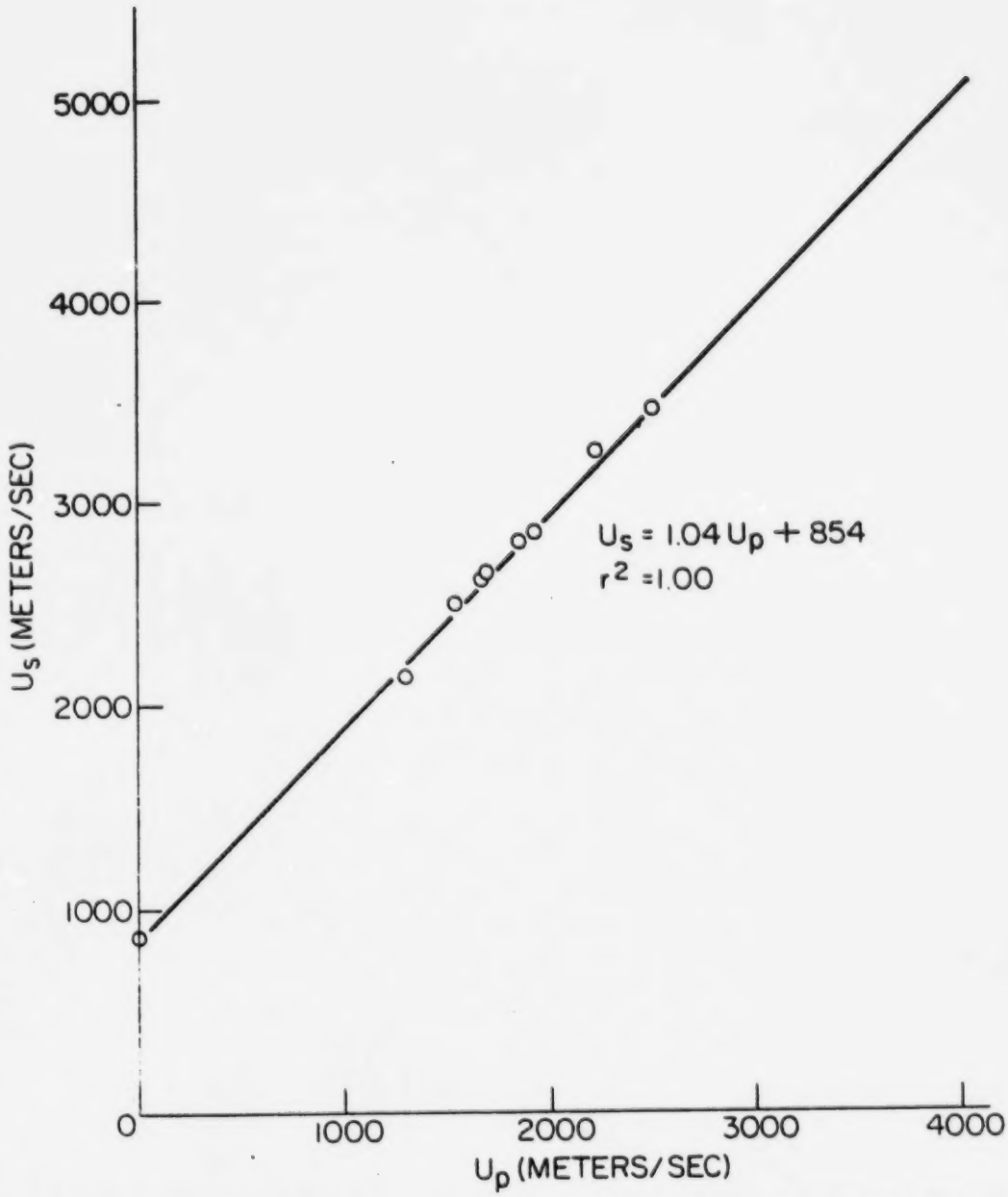


FIGURE 13 SHOCK VELOCITY IS SHOWN AS A FUNCTION OF PARTICLE VELOCITY FOR MOLTEN AMMONIUM NITRATE AT 190° C.

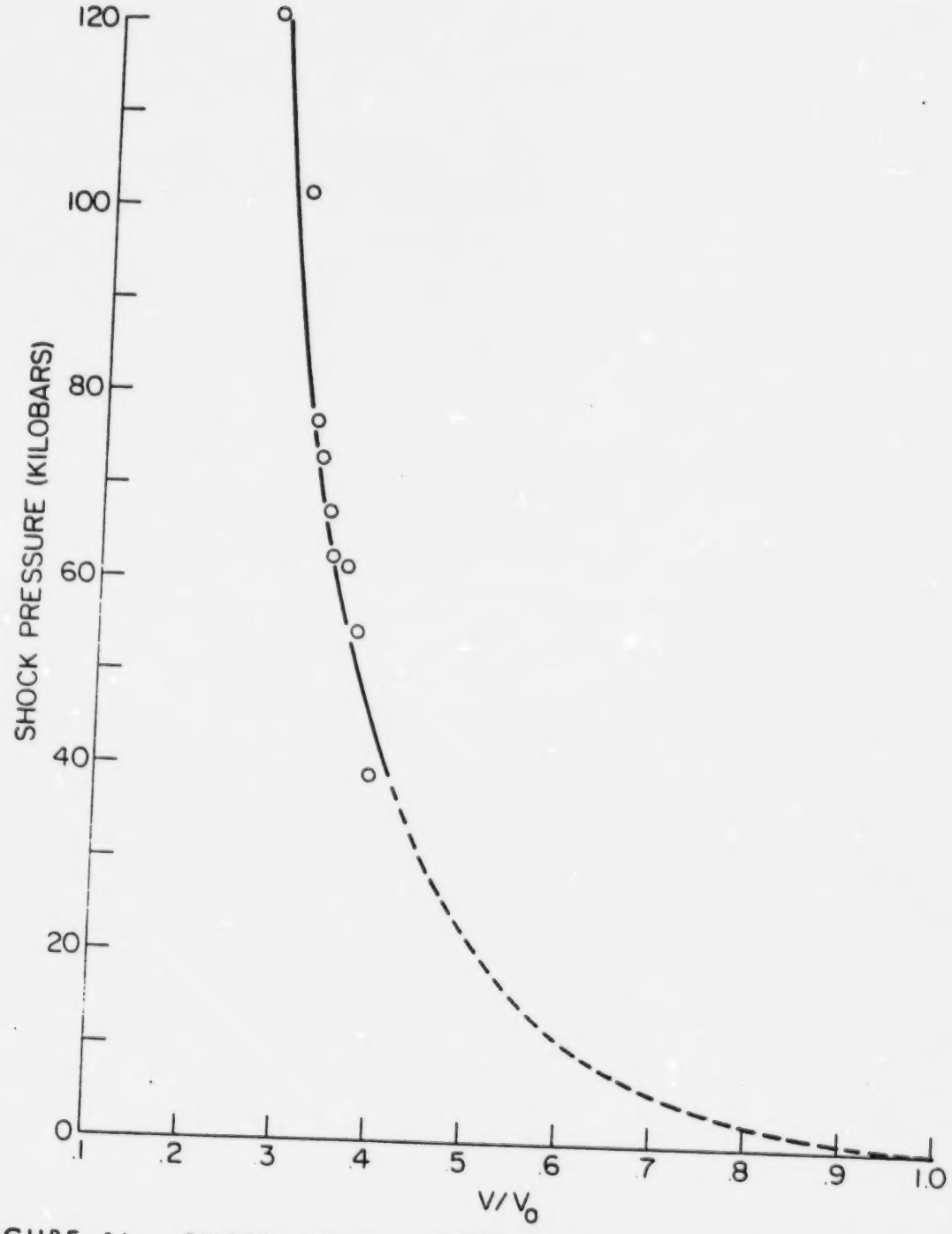


FIGURE 14 EXPERIMENTALLY DERIVED HUGONIOT CURVE FOR MOLTEN AMMONIUM NITRATE AT 190° C.

that, at temperatures exceeding 220°C, the fluid is essentially opaque due to the mass of bubbles migrating to the "surface", which is illdefined.

Defining shock parameters for a heterogeneous fluid consisting of a quiescent fluid and bubbles of thermal decomposition products presents conceptual difficulties. At best, the shock Hugoniots for such materials are useful only for describing the gross hydrodynamic behavior of the heterogeneous mix. The methods of continuum hydrodynamics applied to a discontinuous media will not yield any information on the fine structure of the state variables of the shocked explosive. Also, chemical reaction at or near the shock front must be assumed to be suppressed. These problems notwithstanding, the "macroscopic" Hugoniots were used to establish quantitative shock Hugoniot data at elevated temperatures for the purpose of establishing shock initiation thresholds.

Shock Hugoniots can be constructed by determining any two of the state variables P, V, U_{shock} and $U_{particle}$.
However, by using the technique of Voskobojinikov, et. al (6) it is possible to calculate the particle velocity of a porous substance at its initial density " $\rho_{aerated}$", provided that the particle velocity of the condensed phase, at a given shock pressure, is known. This assumes that the shock pressure is equalized across the shock front

In order to calculate the particle velocity of the condensed phase at elevated temperatures U_{LD}, from that obtained experimentally at

190°C, the following equation is used where the mass fraction of air or gas in the fluid is $<<1$. i.e.

$$\left(\frac{U_{LD}}{U_{190°C}}\right)^2 \cong 1 + \frac{P}{(U_{190°C})^2}\cdot\left(\frac{1}{\rho_{LD}} - \frac{1}{\rho_{190°C}}\right)$$

where U_{LD} is the particle velocity of the condensed phase at elevated temperatures (and hence lower density); $U_{190°C}$ is the experimentally determined particle velocity in the quiescent region at 190°C; P is the corresponding shock pressure; ρ_{LD} is the density of the condensed phase at elevated temperatures resulting from thermal expansion only, and $\rho_{190°C}$ is the density of the fluid at 190°C where $U_{190°C}$ was determined.

Hence, at the same pressure, the ratio of the squares of the particle velocities in the "aerated" and solid substances is

$$\left(\frac{U_{Pa}}{U_{LD}}\right)^2 \quad 1 + \frac{2}{\gamma + 1}\cdot\frac{P}{(U_{LD})^2}\cdot\left(\frac{1}{\rho_{\text{aerated}}} - \frac{1}{\rho_{LD}}\right)$$

where U_{Pa} is the particle velocity of the aerated fluid, γ is the ratio of specific heats of the gaseous decomposition products (here assumed to be 1.285) and ρ_{aerated} is the bulk density of the cavitated fluid. The shock velocity in the aerated fluid can then be calculated from

$$U_{sa} = \frac{P_{\text{shock}}}{\rho_{\text{aerated}} \cdot U_{\text{aerated}}^{\text{particle}}}$$

These calculations are summarized in Table 2 and illustrated graphically in Figure 15.

It should be pointed out that the use of the following equation derived by Voskoboinikov, et al (6), i.e.

$$\left(\frac{U^*}{U}\right)^2 \cong 1 + \frac{P}{U^2}\left(\frac{1}{\rho_{o^*}} - \frac{1}{\rho_o}\right)$$

where the mass fraction of air in the substance in question is much less than 1 by two orders of magnitude, was used to calculate the particle velocity in the fluid at elevated temperatures. In the case of molten ammonium nitrate, this corresponds to

$$\left(\frac{U_{LD}}{U_{190^oC}}\right)^2 \cong 1 + \frac{P}{(U_{190^oC})^2}\left(\frac{1}{\rho_{LD}} - \frac{1}{\rho_{190^oC}}\right)$$

where $_{LD}$ refers to the lowered density resulting from thermal expansion only.

As can be seen in Table 2, the corrections which resulted were very small, ≅ 2% - 3% at 260°C. The use of the particle velocity measured directly from streak photographic records (i.e. Ufs/2, where Ufs is the free surface velocity, Table 1) at 190°C would not be expected to significantly affect the calculation of the particle velocity at elevated temperatures (in a highly aerated state) from Voskoboinikov's other equation, i.e.

$$\left(\frac{U_{Pa}}{U_{LD}}\right)^2 = 1 + \frac{2}{\gamma \pm 1} \cdot \frac{P}{(U_{LD})^2}\left(\frac{1}{\rho_{aerated}} - \frac{1}{\rho_{LD}}\right)$$

TABLE 2

Calculated Shock Data for Molten Ammonium Nitrate at Elevated Temperatures

P_s KBARS/.00987	190°C $U^{190°C\ particle}_{HD}$ m/s	$\rho^{190°C}_{HD}$ gms/cm^3	ρ^{Texp}_{LD} 220 gms/cm^3	Texp $U^{particle}_{LD}$ m/s	ρ^{Texp}_{aer} 220 gms/cm^3	Texp $U^{particle}_{aer}$ m/s	Texp U^{shock}_{aer} m/s
39,000/(.00987)	1304	1.415	1.395	1319	1.395	1319	2147
54,400/(.00987)	1558	1.415	"	1576	"	1576	2507
61,300/(.00987)	1672	1.415	"	1691	"	1691	2633
62,300/(.00987)	1694	1.415	"	1713	"	1713	2642
67,200/(.00987)	1779	1.415	"	1798	"	1798	2714
72,900/(.00987)	1865	1.415	"	1885	"	1885	2808
76,900/(.00987)	1929	1.415	"	1949	"	1949	2865
101,600/(.00987)	2242	1.415	"	2265	"	2265	3258
121,300/(.00987)	2513	1.415	"	2538	"	2538	3472
			230		230		
39,000/(.00987)	1304	1.415	1.388	1325	1.375	1336	2155
54,400/(.00987)	1558	1.415	"	1582	"	1592	2517
61,300/(.00987)	1672	1.415	"	1697	"	1708	2644
62,300/(.00987)	1694	1.415	"	1719	"	1730	2653
67,200/(.00987)	1779	1.415	"	1805	"	1816	2726
72,400/(.00987)	1865	1.415	"	1902	"	1904	2821
76,400/(.00987)	1929	1.415	"	1956	"	1968	2879
101,600/(.00987)	2242	1.415	"	2273	"	2287	3274
121,300/(.00987)	2513	1.415	"	2546	"	2561	3490
			240		240		
39,000/(.00987)	1304	1.415	1.382	1329	1.310	1380	2186
54,400/(.00987)	1558	1.415	"	1588	"	1647	2555

TABLE 2 (continued)

61,300/(.00987)	1672	1.415	1.382	1703	1.310	1765	2686
62,300/(.00987)	1694	1.415	"	1725	"	1788	2695
67,200/(.00987)	1779	1.415	"	1811	"	1875	2771
72,900/(.00987)	1865	1.415	"	1898	"	1965	2870
76,900/(.00987)	1929	1.415	"	1963	"	2031	2929
101,600/(.00987)	2242	1.415	"	2280	"	2358	3333
121,300/(.00987)	2513	1.415	"	2554	"	2636	3558
			250		250		
39,000/(.00987)	1304	1.415	1.375	1335	1.16	1499	2272
54,400/(.00987)	1558	"	"	1594	"	1786	2660
61,300/(.00987)	1672	"	"	1710	"	1912	2800
62,300/(.00987)	1694	"	"	1732	"	1935	2812
67,200/(.00987)	1779	"	"	1818	"	2027	2896
72,900/(.00987)	1865	"	"	1905	"	2122	3001
76,900/(.00987)	1929	"	"	1970	"	2191	3066
101,600/(.00987)	2242	"	"	2289	"	2540	3493
121,300/(.00987)	2513	"	"	2563	"	2832	3742
			260		260		
39,000/(.00987)	1304	1.415	1.368	1340	0.8	1895	2606
54,400/(.00987)	1558	"	"	1600	"	2257	3061
61,300/(.00987)	1672	"	"	1717	"	2402	3233
62,300/(.00987)	1694	"	"	1739	"	2427	3251
67,200/(.00987)	1779	"	"	1825	"	2534	3358
72,900/(.00987)	1865	"	"	1912	"	2648	3486
76,900/(.00987)	1929	"	"	1977	"	2729	3568
101,600/(.00987)	2242	"	"	2297	"	3155	4079
121,300/(.00987)	2513	"	"	2572	"	3492	4399

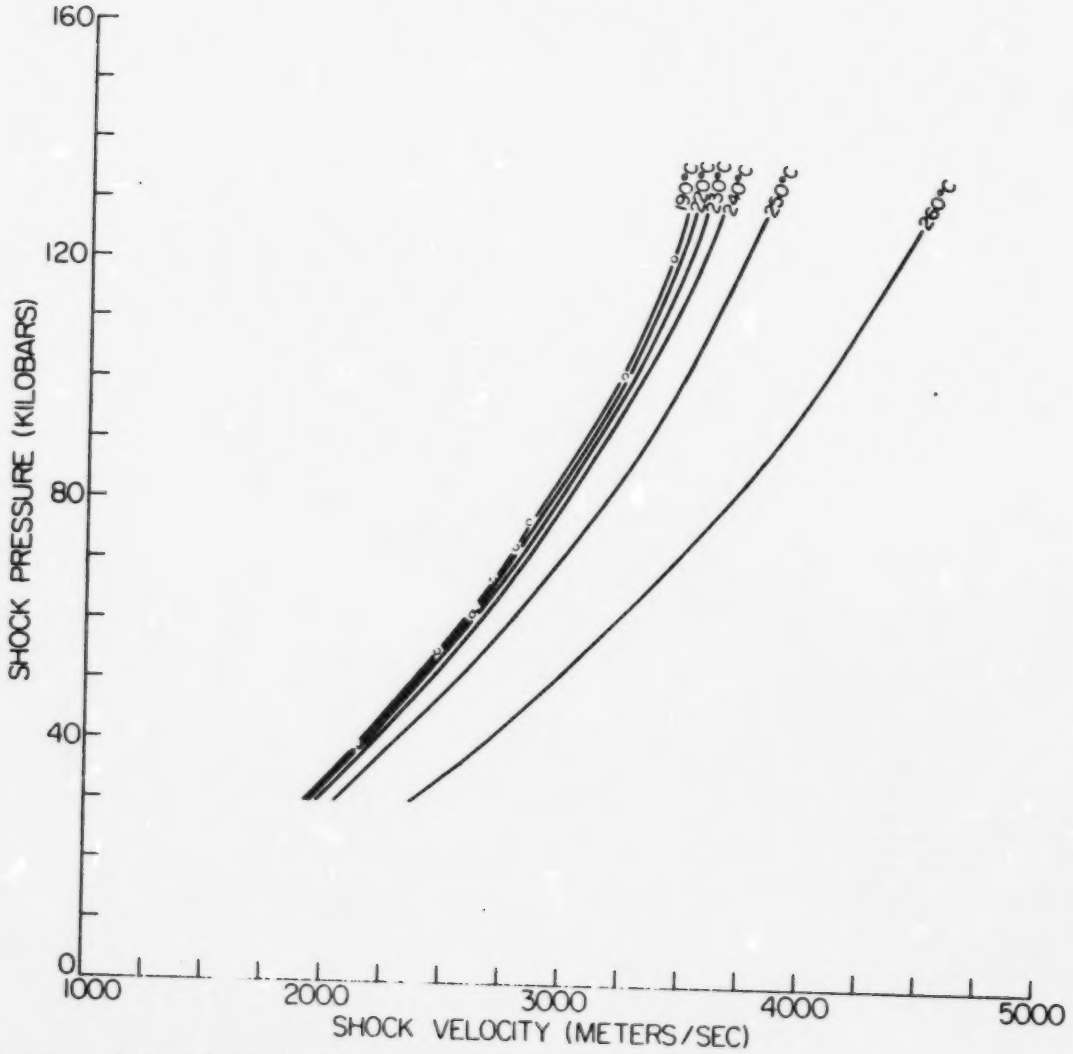


FIGURE 15 EXPERIMENTALLY DERIVED (190° C) AND CALCULATED RELATIONSHIPS (T > 190° C) BETWEEN SHOCK PRESSURE AND SHOCK VELOCITY FOR MOLTEN AMMONIUM NITRATE.

DISCUSSION

A comparison of shock pressure-shock velocity data between fluids of comparable densities, as determined by Cook et. al (7) , and molten ammonium nitrate at 190°C, shows general agreement to within 15%-20%. These fluids do not have the same dynamic compressibilities, however.

The sources of experimental error in determining shock and free surface velocities are: planar shock wave curvature (± .01 μs); uncertainty in record analysis (0.1% to 0.5% of U_{shock} and $U_{free\ surface}$ depending on record quality which is in turn a function of film shrinkage, etc.) specimen density variation (± .5% since it is impossible to determine the temperature to much greater precision than ±2C°), and effects of some chemical reaction on shock velocity measurements. However, the growth of chemical reaction produces an increase in the shock-wave velocity for increasing explosive thickness, and this manifests itself by an abrupt increase in the slope of the streak camera record. This was not in evidence throughout the test series.

It is possible, of course, that isolated sites of chemical reaction could have resulted from the sudden impact of the shock wave. If so, during shock transit times (< 1 μsecond) such reactive sites might be expected to contribute only to a smalldegree, i.e. 1%-2% or less, to the

energy of the shock. Since the shock-velocity-particle velocity relation was linear, this is taken as sufficient indication that these measurements are essentially free of reaction effects.

The general direction of development of an equation of state is not to provide data for the calculation of shock temperatures or other shock Hugoniot data other than shock pressures and corresponding shock velocities at that particular density.

In explosives whose energy yield upon detonation is quite low compared to energetic liquid explosives such as nitroglycerine, the determination of shock temperatures is not critical. These lower yield explosives will tend to rely to a greater extent upon "macro" hot spots as opposed to "micro" hot spots, the latter being sufficient to initiate an explosive state of decomposition in high energy yield liquid explosives.

Thus it is necessary to know only two critical parameters, shock pressure and shock velocity as a function of density, to be able to correlate shock velocity with critical impact pressures, i.e. those pressures which are necessary to establish shock initiation thresholds.

In order to be able to delineate those critical impact pressures which can induce detonations over a temperature range of 220°C to 260°C, a precision of 3% to 5% in determination of these pressures is acceptable. This approach to examining how explosives, which are in the process of being thermally decomposed, become more shock sensitive is unique, in that attemps to quantify those critical impact pressures

generally are not done. Rather, greater use is made of a variety of impact tests which have been standardized by institutions such as the U.S. Bureau of Mines or Picatinny Arsenal.

Consequently it is not possible to readily cross check these results with that of other workers. However, it is felt that this approach will yield data which lends itself to much more practical applications such as design of buildings or stowage containers.

CONCLUSION

The shock pressure as a function of shock velocity has been determined for molten ammonium nitrate at 190°C where ρ_o = 1.42gms/cm^3. Shock velocities up to ≈3500 meters/second and resulting shock pressure up to ≈ 120 kilobars were used to establish shock velocity-shock pressure data for use in elevated temperature regions (i.e. up to 260°C), at which point the shock sensitivity of molten ammonium nitrate is exceedingly high, and approaches that of nitroglycerine based dynamites.

The relationship between shock velocity and particle velocity was established for molten ammonium nitrate at 190°C and found to be linear over the range of shock velocities examined.

The Rankine-Hugoniot curve for molten ammonium nitrate at 190°C was also established.

These calculated parameters at elevated temperatures permit determination of critical impact pressures as a function of temperature once the shock velocity in the fluid is known.

It should be pointed out, however, that determination of these parameters is not a function of charge diameter. However, critical impact pressures are a function of diameter. Consequently, any shock initiation (card gap) work should be conducted at a large enough practical charge diameter, such that any further increase in charge diameter will not appreciably affect the results.

It is therefore possible, on the basis of results obtained, to quantify those shock pressures and shock velocities which can initiate detonations in molten ammonium nitrate, especially at elevated temperatures.

3. CARD GAP TEST DATA FOR MOLTEN AMMONIUM NITRATE

In order to determine the magnitude of the critical shock pressures and shock or particle velocities in molten ammonium nitrate, a calibrated card gap test was designed.

Plexiglass, which has true shock wave transmission characteristics, was used as the attenuator for the explosively derived shock. The shock velocity in the plexiglass wafers was calibrated as a function of wafer thickness using a streak camera photographic technique.

C-4 was used as the explosive donor. The molten ammonium nitrate was contained in a 125 millimeters I.D. pyrex glass tube 400 milimeters in length to accomodate all of the critical diameters which molten ammonium nitrate exhibits over a temperature range of 220°C to 260°C.

Since the shock Hugoniots for molten ammonium nitrate have been determined, critical shock initiation parameters in the molten ammonium nitrate were determined using a planar shock reflection technique.

RESULTS

Data showing the relationship between the logarithm of Plexiglass wafer thickness and temperature in the molten ammonium nitrate is shown in Figure 16. A best fit line was drawn between the "GO/NO-GO" points to delineate that region where the probability of a detonation was high, from that region where the probability of detonation failure was also high. With the thermocouples used, it was not possible to remotely sensor the temperature with a precision greater than $\pm$ 2C°.

The shock velocity at the free surface of the Plexiglass wafer was determined photographically from a streak camera record. The relationship between Plexiglass shock velocity and Plexiglass wafer thickness is shown in Figure 17. The shock velocity is very rapidly attenuated in Plexiglass, dropping off to a level of ≈3000 meters/second after 10 centimeters, remaining essentially constant at ≈ 2800 - 2900 meters/second out to 20 centimeters. The velocity of sound in Plexiglass has been determined by various workers to be ≈ 1900 - 2100 meters/second. The biggest source of error in measuring the shock velocities from a photographic record, is determining the tangent of the angle θ between the free surface on the streak photographic record and the tangent to the streak photographic record of the shock velocity at the free surface, as shown in Figure 18. This limit of error has been estimated to be $\pm$5%.

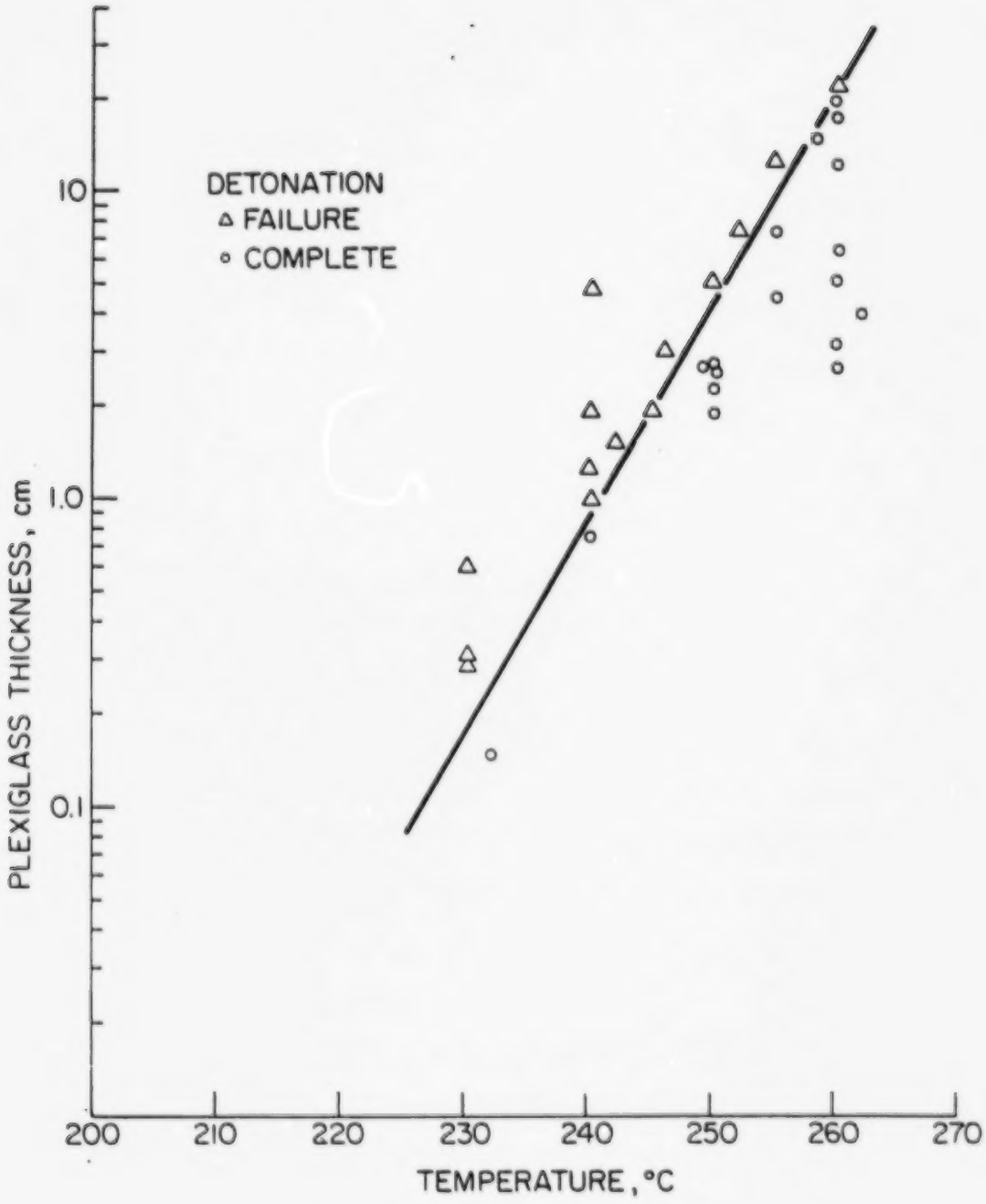


FIGURE 16 THE RELATIONSHIP BETWEEN THE LOGARITHM OF PLEXIGLASS WAFER THICKNESS AND TEMPERATURE IN THE MOLTEN AMMONIUM NITRATE IS SHOWN. A BEST FIT LINE DELINEATES THOSE REGIONS OF A HIGH PROBABLITY OF DETONATION FROM THOSE REGIONS WHERE THE PROBABLITY OF DETONATION IS LOW.

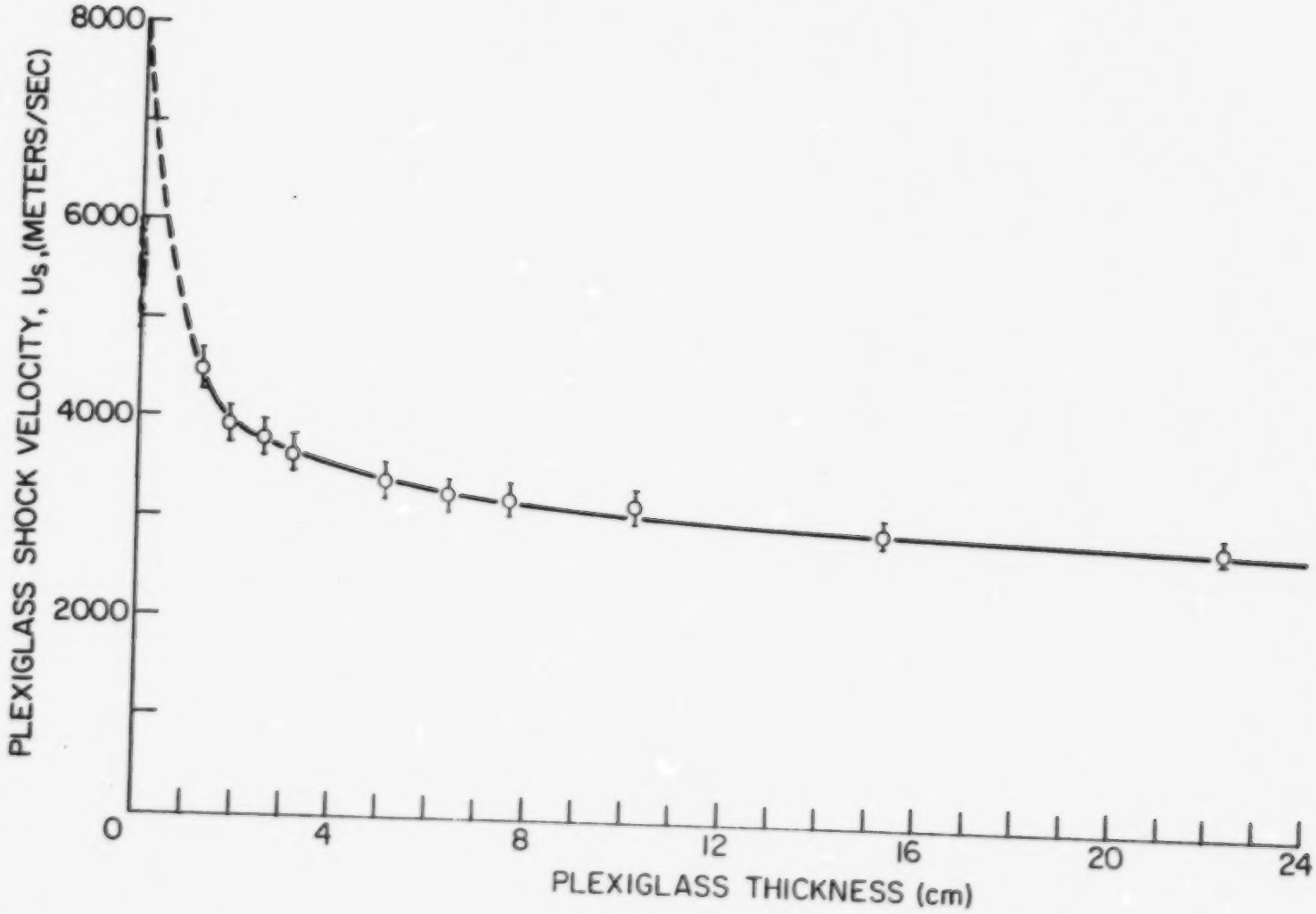
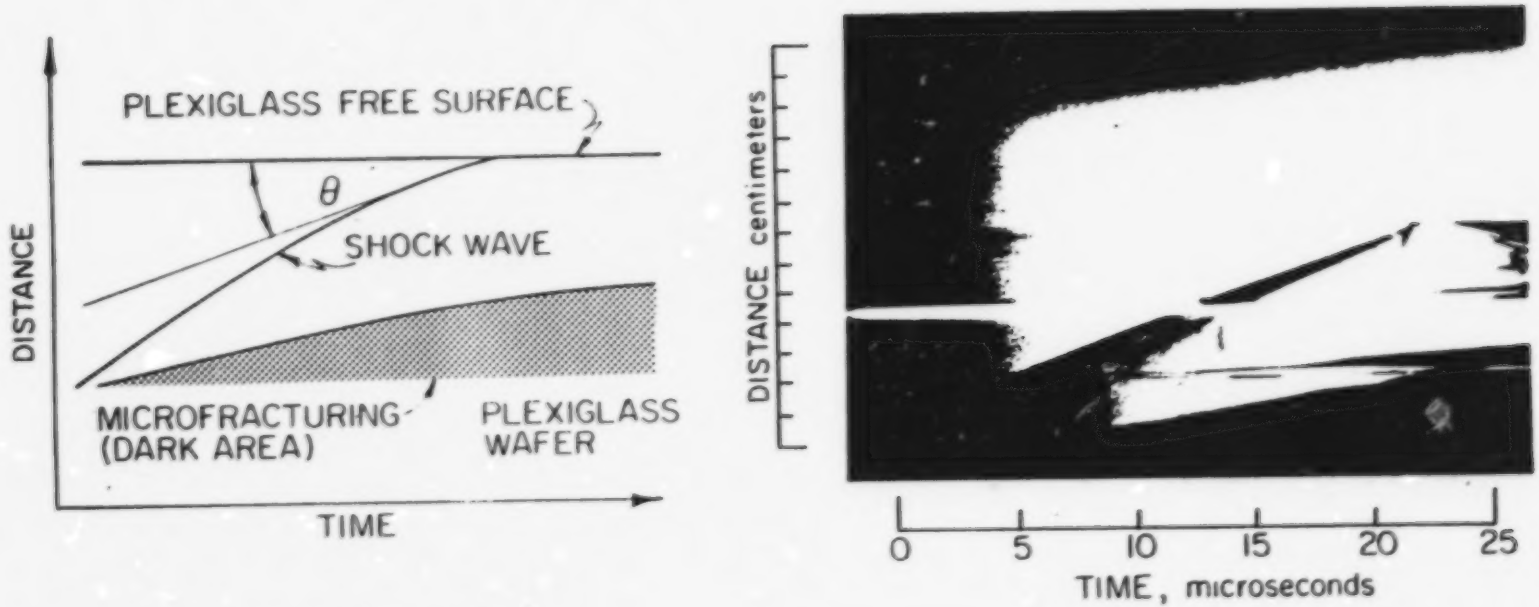


FIGURE 17 PLEXIGLASS SHOCK VELOCITY IS SHOWN AS A FUNCTION OF PLEXIGLASS WAFER THICKNESS, AS DETERMINED BY STREAK PHOTOGRAPHIC RECORDS.



$V\ (mm/\mu s) \quad R.M.W.\ \tan\theta$

where R SCALE REDUCTION FACTOR
M ENLARGEMENT MAGNIFICATION
W STREAK CAMERA WRITING RATE IN mm, μs

FIGURE 18 TYPICAL STREAK TRACE OF A SHOCK WAVE IN PLEXIGLASS IS SHOWN WITH SCALED DIAGRAM ILLUSTRATING SHOCK PROCESS.

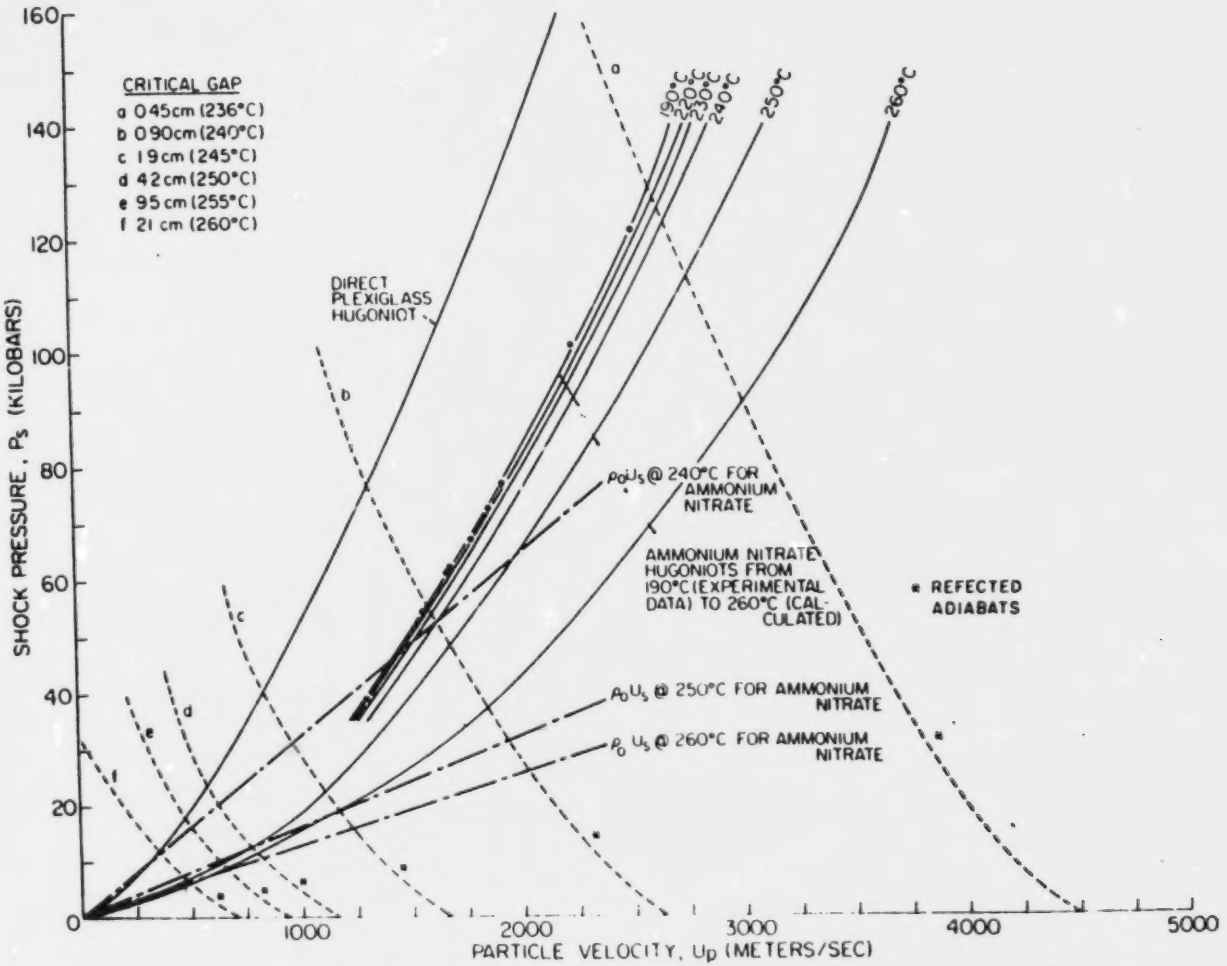


FIGURE 19 THE PRESSURE - PARTICLE VELOCITY HUGONIOTS FOR PLEXIGLASS AND MOLTEN AMMONIUM NITRATE ARE PLOTTED ON THE SAME PLANE. THE REFLECTED PLEXIGLASS ADIABATS INTERCEPT THE DIRECT HUGONIOTS FOR MOLTEN AMMONIUM NITRATE AT CRITICAL GAP.

DISCUSSION

From a knowledge of the critical gap shown in Figure 16, the thickness of Plexiglass necessary to suppress initiation of detonation in molten ammonium nitrate can be estimated. This thickness can then be correlated with shock velocity as shown in Figure 17, which can then be correlated with the shock Hugoniot for Plexiglass to determine shock Pressure. † Since shock pressure, shock velocity and density are known, the particle velocity can then be determined for a particular shock velocity.

Therefore, by plotting both the Hugoniot for Plexiglass and the Hugoniots for molten ammonium nitrate (which are themselves functions of temperature) as a function of particle velocity, it is possible to determine critical impact pressures and critical particle velocities from the intercept of the reflected adiabats for Plexiglass and the direct shock Hugoniots for molten ammonium nitrate, as shown in Figure 19. The critical shock initiation data for molten ammonium nitrate at 230°C, 240°C, 250°C and 260°C is summarized in Table 3 below. Critical impact pressures and critical particle velocities are shown in Figures 20 and 21 where they are plotted as a function of temperature.

---

† The equation of state for the Plexiglass used in this test series was determined and the shock Hugoniot data plotted on the same graph as the smoothed data curve developed by Cook, Keyes and Ursenbach (8)

as shown in Figure 22. The smoothed data for Plexiglass did not differ significantly from the Hugoniot data derived in this test series, and the smoothed data was used in the determination of the Plexiglass shock pressures and particle velocities.

Table 3

Critical Shock Parameters for Molten Ammonium Nitrate

T°C	ρ_o Grams/ cm^3	Critical Gap, cm	Plexiglass Shock Velocity Meters/Second	Plexiglass Shock Pressure Kilobars	Ammonium Nitrate Critical Impact Pressure, KBars	Ammonium Nitrate Critical Particle Velocity Meters/ Second
230	1.37	.18	7250	>200	Off Scale	Off Scale
235	1.35	.45	6250	164	125	2645
240	1.32	.9	5000	76	52	1625
245	1.25	1.9	3950	34	24	1085
250	1.16	4.2	3500	24	13	775
255	1.05	9.5	3125	18	9.5	650
260	.8	21.0	2850	12	6.5	487
190	0.95 (Glass Bubbles)	>13 <15	>2950 <3000	≈15	≈ 8	≈ 550

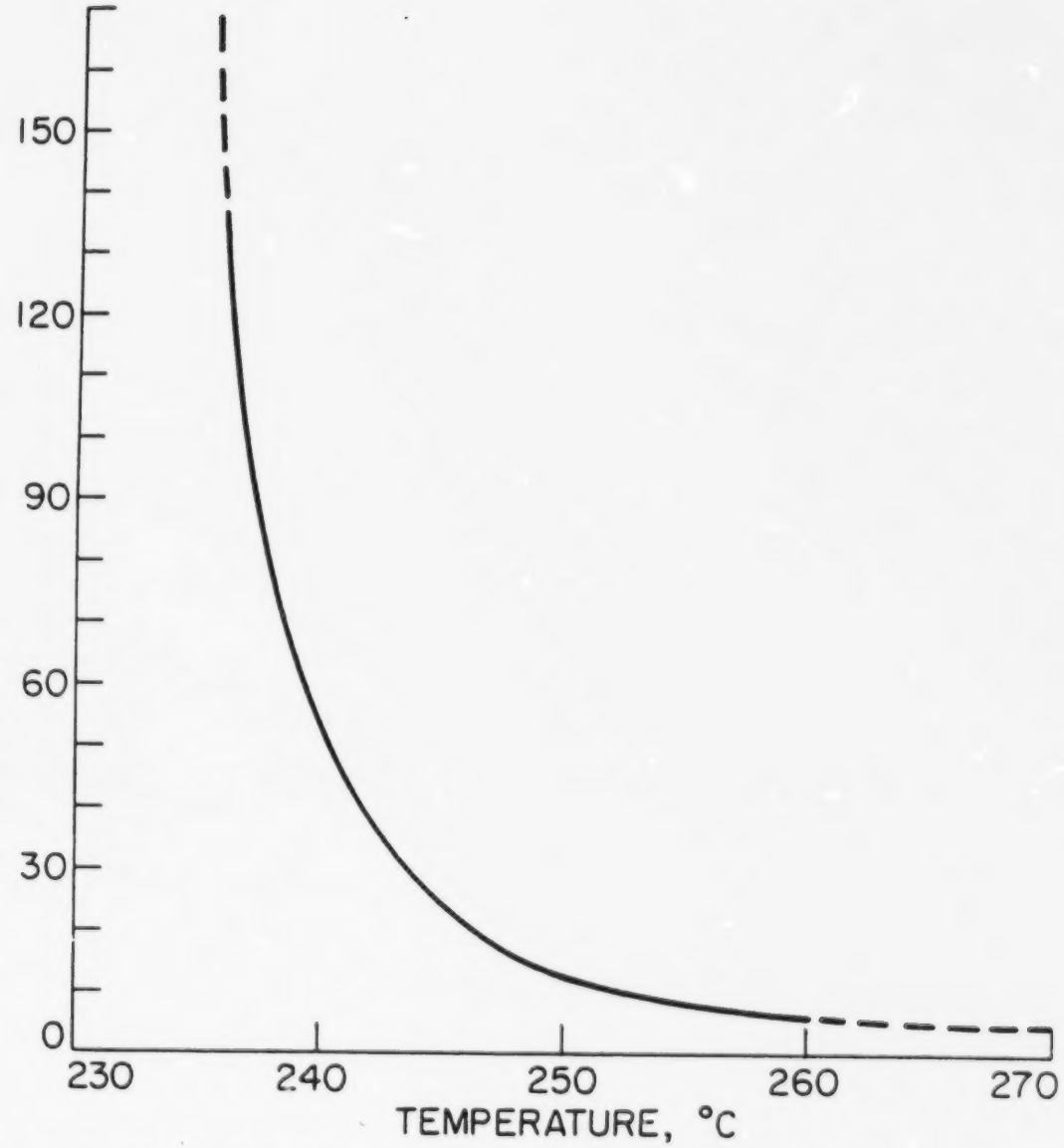


FIGURE 20 CRITICAL IMPACT PRESSURE FOR MOLTEN AMMONIUM NITRATE IS SHOWN AS A FUNCTION OF TEMPERATURE.

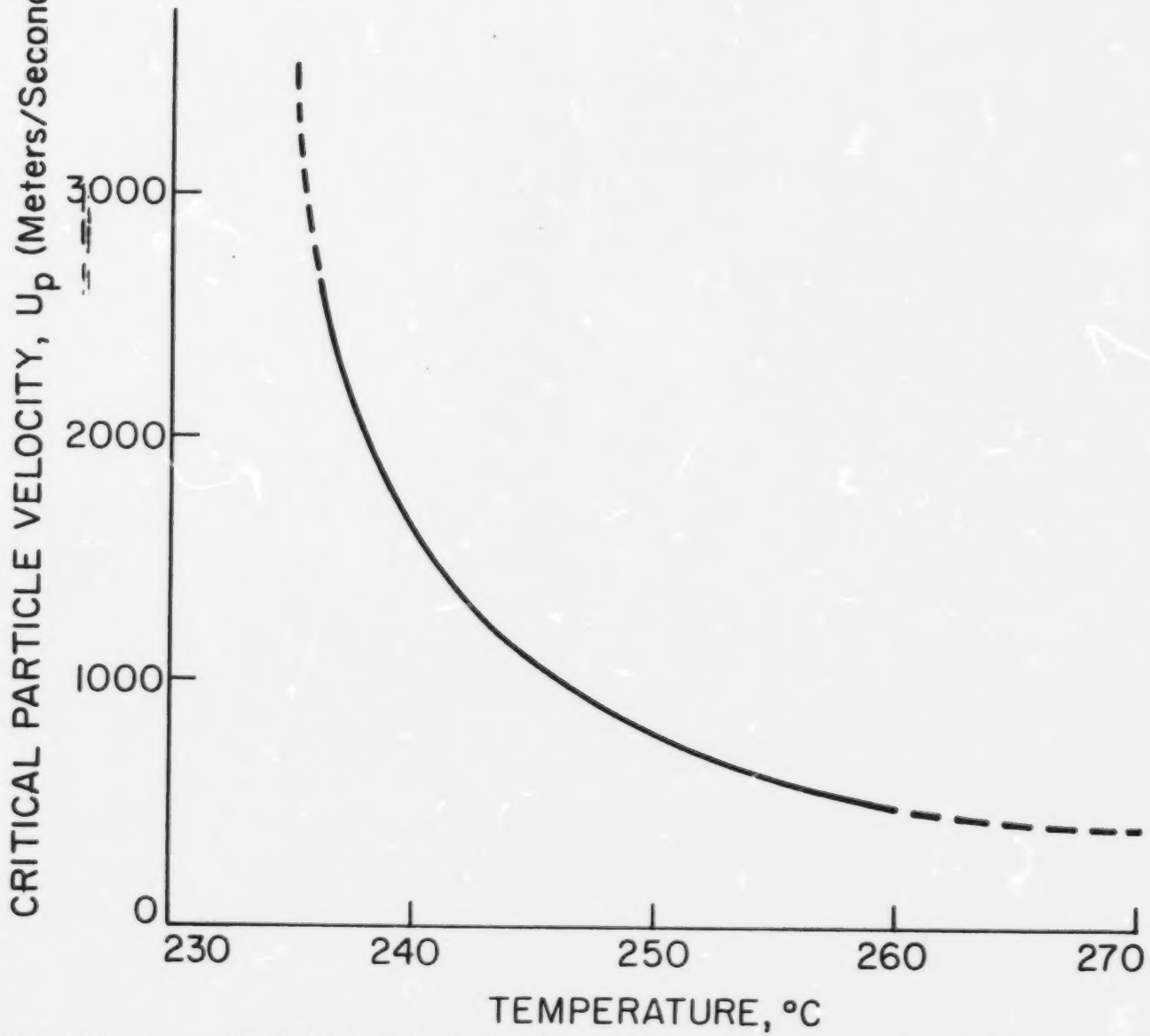


FIGURE 21 CRITICAL PARTICLE VELOCITY FOR MOLTEN AMMONIUM NITRATE IS SHOWN AS A FUNCTION OF TEMPERATURE.

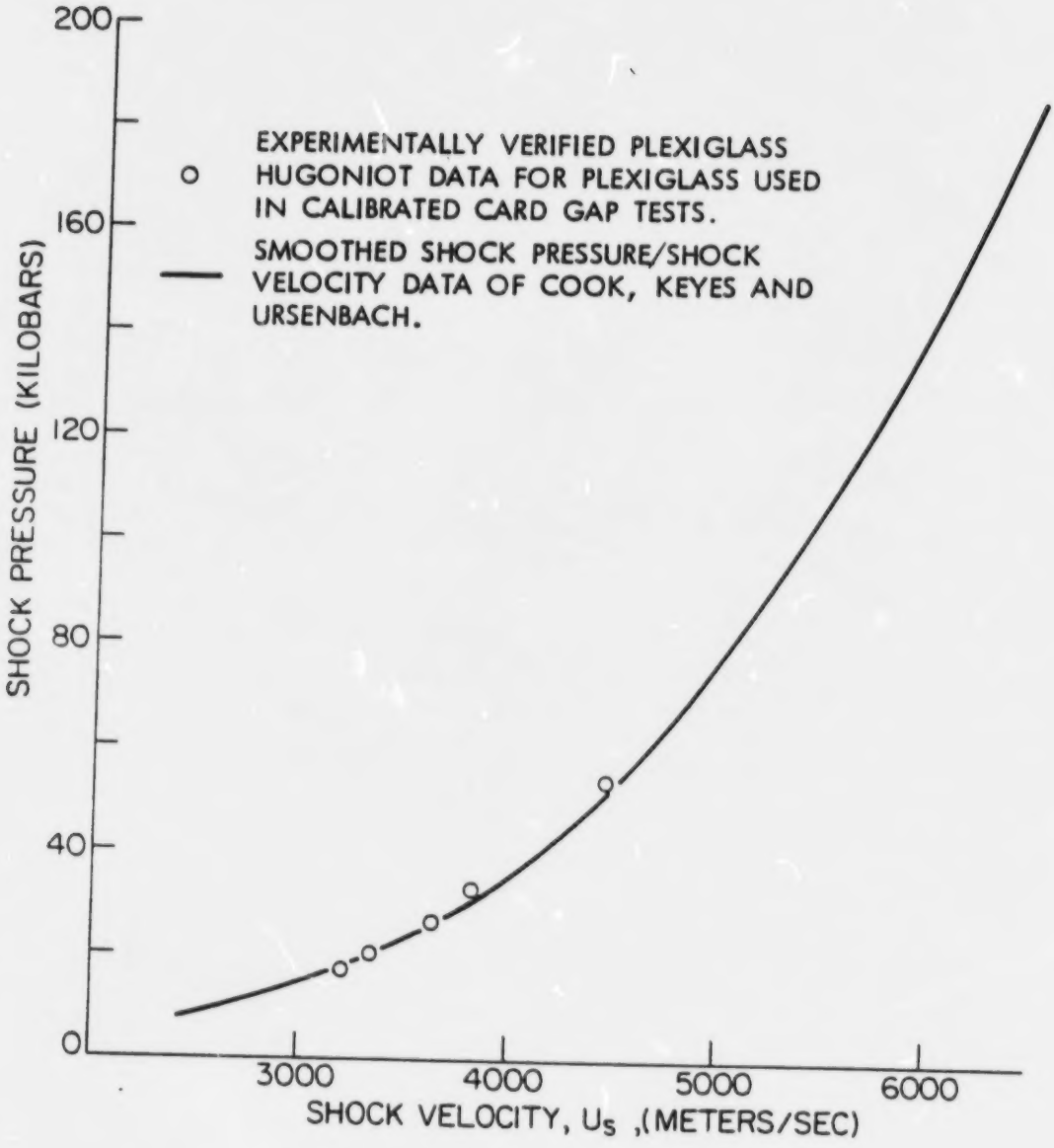


FIGURE 22: EXPERIMENTALLY VERIFIED PLEXIGLASS HUGONIOT DATA IS SHOWN WITH SMOOTHED SHOCK PRESSURE/SHOCK VELOCITY DATA OF COOK, KEYES AND URSENBACH (1962).

The shock sensitivity of molten ammonium nitrate increases at an almost exponential rate once the material is heated past ≈ 230°C. At temperatures greater than 245°C the shock sensitivity is quite high, an impact pressure of approximately 6-7 Kilobars in the fluid being sufficient to initiate the molten material at ≈ 260°C. Shock initiation pressures this low may present a hazard from the point of view of accidental initiation by flying plates, or projectile impact. The U.S. Bureau of Mines (9) conducted a series of Projectile Impact Initiation Tests on several commercial and military explosives, including several cryogenic explosives such as liquid hydrogen/solid oxygen and liquid oxygen/solid butane. Nitroglycerine/ethylene glycol dinitrate mixtures (50/50) were also tested. Peak shock initiation pressures of the order of 1 Kilobar were determined for the cryogenic mixtures and 3 Kilobars for the nitroglycerine/ethylene glycol dinitrate mixtures.

The shock velocities recorded for Plexiglass as a function of wafer thickness show no discrepancies when compared to similar work conducted by Cook (8) and the terminal velocities recorded at large gaps show general agreement with that of other workers (10).

Card gap work has been conducted on various types of industrial and military explosives by the U.S. Bureau of Mines (11) although not in an apparatus of the dimensions encountered in this test apparatus.

In order to establish a relative comparison between the shock sensitivity of molten ammonium nitrate at 260°C and other explosives, the following explosives were also tested at the same gap level which just failed to detonate molten ammonium nitrate at 260°C, i.e. 22.6 centimeters of Plexiglass, and in the same charge geometry as used in these tests with molten ammonium nitrate:

1) Powermex 500 (an ethylene glycol mononitrate sensitized small diameter slurry explosive);
2) PowerFrac 75% (a nitroglycerine based dynamite);
3) Nitromethane sensitized with 5% by weight of ethylene diamine.

In this test series only the PowerFrac 75% dynamite initiated at this gap level, and showed a long lead time to establish a stable detonation.

The temperature dependence of the critical shock parameters is actually a density dependence and was amply demonstrated by doing a series of card gap tests on molten ammonium nitrate at 190°C. The difference was that the molten ammonium nitrate at 190°C was blended with glass bubbles (hollow glass spheres or microballoons) which have the following properties:

Nominal Bulk Density - 0.10 grams/cm^3

Size - 90% by volume between 20 and 130 microns

Nominal Diameter - 90 microns

Wall Thickness - ≈ 0.5 microns

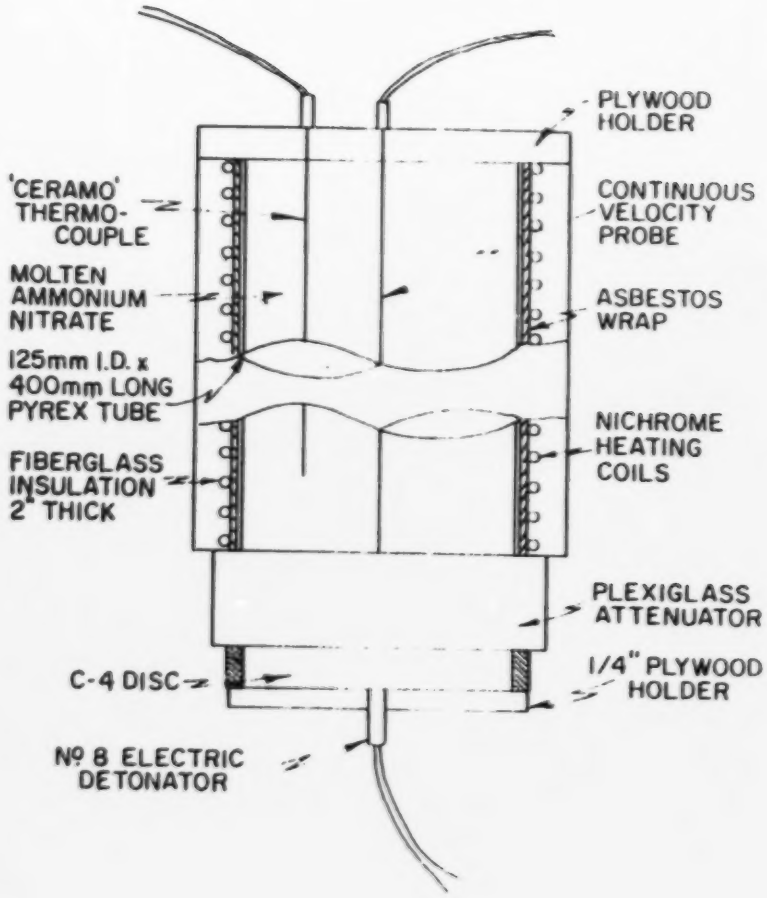
In order to bring the bulk density of ammonium nitrate at 190°C from 1.42 grams/cm^3 down to what it would be at 250°C - 260°C, i.e. 0.8 grams/cm^3 to 0.95 grams/cm^3, glass bubbles of the above specifications (3M Brand, Type B15/250) were blended in, at a ratio of 5.5 grams of glass bubbles per 100 grams of ammonium nitrate. This resulted in a bulk density of ≈ 0.95 grams/cm^3.

From the thermal decomposition data the temperature corresponding to this bulk density which would normally result from thermal decomposition alone, is 255°C to 257°C.

As shown in Figure 16, ammonium nitrate in this temperature range requires a thickness of Plexiglass of approximately 10 cm - 15 cm in order to attenuate an explosively derived shock of the type generated in the apparatus previously described.

This mixture, which requires constant stirring, was tested in this apparatus shown in Figure 23 using a C-4 explosive donor. The mixture initiated at 190°C when a 10 cm thickness of Plexiglass was used, but failed when a 15 cm thickness of Plexiglass was used. The mixture also initiated when a thickness of Plexiglass of ≈ 13 cm was used. From the data in Figure 16, this correlates very closely with the critical gap at 255°C to 257°C.

This mixture also initiated with a #8 Electric Blasting Cap when tested in an apparatus of the type shown in Figure 24.



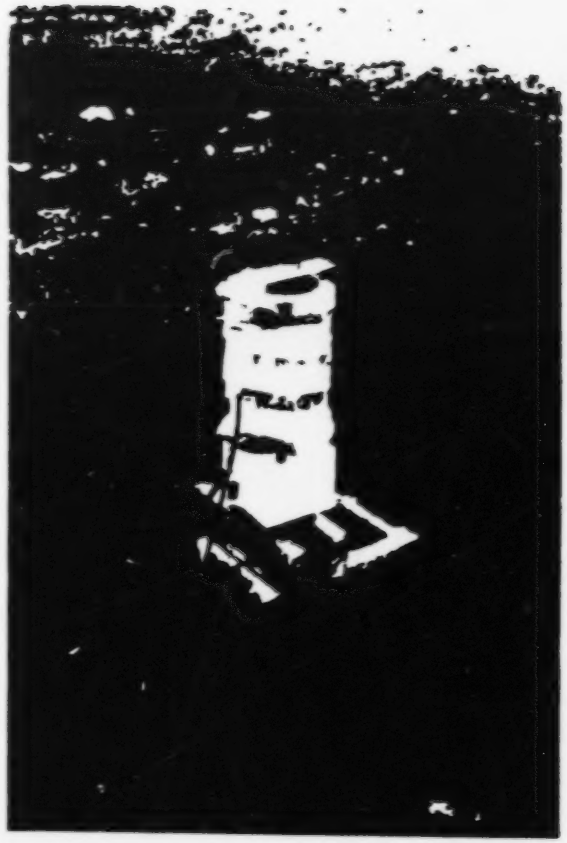
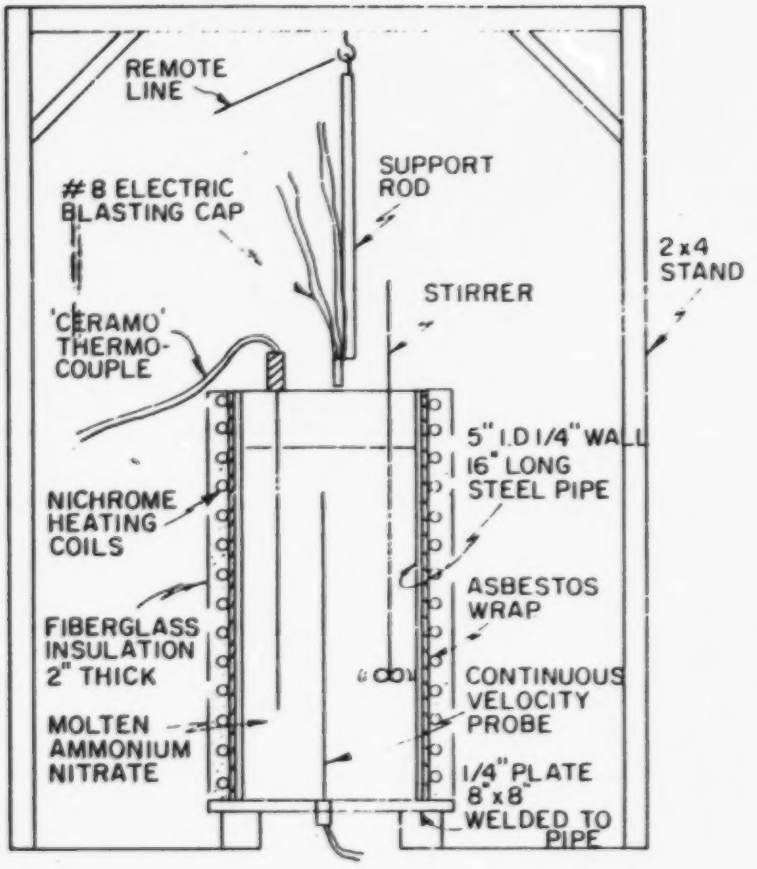


FIGURE 23: APPARATUS USED TO DETERMINE CRITICAL GAP VALUES FOR MOLTEN AMMONIUM NITRATE AS A FUNCTION OF TEMPERATURE IS SHOWN WITH ITS CROSS SECTIONAL DRAWING.



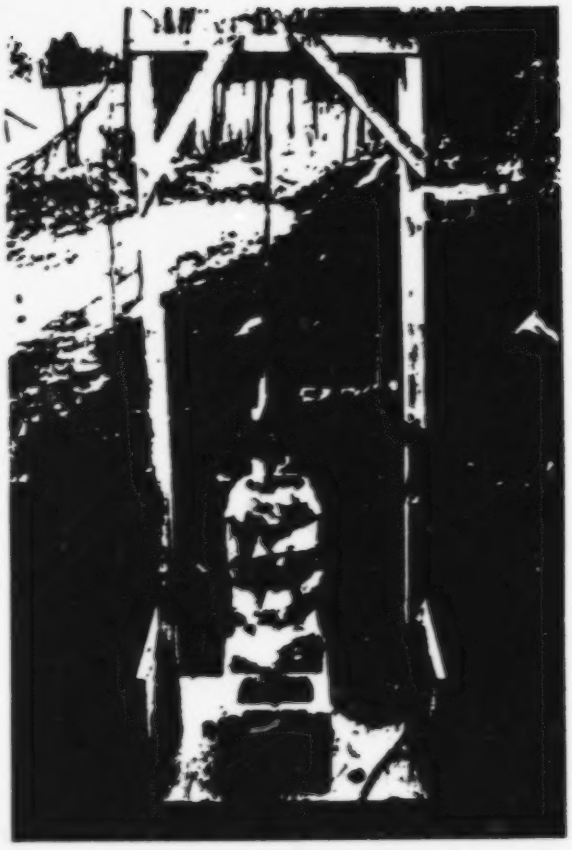


FIGURE 24 APPARATUS USED TO INITIATE MOLTEN AMMONIUM NITRATE/GLASS BUBBLES AT 190° C WITH A #8 BLASTING CAP IS SHOWN WITH ITS SCHEMATIC DIAGRAM.

A detonation velocity of ≈ 1500 meters/second was observed for both tests, which agrees well with typical velocity of detonation data recorded for molten ammonium nitrate at 260°C.

CONCLUSION

Critical shock parameters for chemically pure molten ammonium nitrate (i.e. critical impact pressure and critical particle velocity) were determined over a temperature range from 230°C to 260°C.

Critical impact pressure was found to vary from 125 Kilobars at 236°C to 6.5 Kilobars at 260°C. A critical impact pressure of ≈ 6.5 Kilobars puts molten ammonium nitrate at 260°C and greater, in the same class of shock sensitivity as nitroglycerine and/or nitroglycerine based dynamites.

From a series of tests using glass bubbles to stimulate at 190°C the same density molten ammonium nitrate has at 260°C, the shock sensitivity of molten ammonium nitrate was found to be a strong function of density and not necessarily a function of temperature.

The exponential increase in shock sensitivity of molten ammonium nitrate to a high level may indicate a hazardous state under conditions of fire exposure. This high shock sensitivity also gives some indication that building structures used to bulk store ammonium nitrate or ammonium nitrate fertilizers should be very lightly constructed in order to prevent massive collapse of the burned out structure on to semi-confined pools of molten ammonium nitrate which may have collected.

The ammonium nitrate tested here is the chemically pure material. Future work should investigate if shock sensitivity is affected by

organic contaminants or contaminants known to accelerate thermal decomposition at lower temperatures, such as chromium compounds and other transition metals.

Fertilizer grade ammonium nitrate is often coated with anti-caking agents, many of which are surface active agents. These surfactants can and do cause considerable "foaming" when the fertilizers are melted and thermally decomposed. Such "aeration" could substantially affect the shock sensitivity by simultaneously lowering the bulk density and acting as a fuel.

4. DETONATION CHARACTERISTICS OF MOLTEN AMMONIUM NITRATE

INTRODUCTION

Apart from its aqueous solutions, ammonium nitrate exists in two forms, the solid phase, such as prilled ammonium nitrate, and the liquid phase, or molten state, which is encountered at temperatures greater than 169°C for the chemically pure material.

The work described herein deals with the detonation characteristics of the molten material only, and not the aqueous solutions.

All tests were done on the chemically pure ammonium nitrate and not on fertilizer grade ammonium nitrate.

The detonation characteristics of molten ammonium nitrate were studied over a temperature range of ≈ 180°C to 260°C as follows:

a) density determinations of the liquid phase system over a temperature range of 175°C to 260°C;

b) determination of critical primer weights and types necessary to initiate a stable detonation in the molten material as a function of temperature;

c) critical diameter determinations on confined and unconfined systems as a function of temperature;

d) velocity of detonation studies as a function of temperature and diameter;

e) sonic velocity determinations in the liquid phase system over a temperature range from 170°C to 260°C.

1. DENSITY DETERMINATIONS FOR MOLTEN AMMONIUM NITRATE FROM 170°C TO 260°C.

Liquid phase ammonium nitrate differs from most other liquid explosives in that its bulk density is a strongly dependent function of temperature, due to the fact that increases in temperature well above 169°C not only results in thermal expansion of the fluid, but decomposition into N_2O and H_2O, and dissociation into NH_3 and HNO_3 as well.

In addition to undergoing density changes as a result of thermal decomposition, products tend to "aerate" the fluid, resulting in a cavitated state. At temperatures greater than 210°C, the decomposition and dissociation becomes significant, and the reactions proceed as follows:

1) $NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$ $\quad \Delta H_g = 38.3$ Kcals/mole

$\Delta H_s = 41.7$ Kcals/mole

2) $NH_4NO_3 \rightarrow N_2O + 2H_2O$ $\quad \Delta H_{H2O}$ gas $= -13.2$ Kcals/mole

ΔH_{H2O} liquid $= -33.1$ Kcals/mole

As temperatures approach 260°C, gas evolution becomes very rapid, and the liquid appears to "boil" violently.

Since the density is obviously a very important function of temperature, so then are the detonation properties of the cavitated fluid. Consequently, before any real conclusions can be drawn from measurements of detonation parameters and phenomena, the density as a function of temperature must be determined.

2. THEORY

According to Cook and Abegg (12), the decomposition of pure ammonium nitrate accurately obeys first order reaction kinetics. They determined the first order constant k in 1956 by weight loss measurements, but they, like Robertson (13), made no correction for the weight loss due to dissociation (evaporation). It is known, however, that N_2O and H_2O are accompanied in the products by NH_3 and HNO_3 at their equilibrium pressure. Cook and Abegg's rate constants for total weight loss over the range 217 to 267°C obeyed the equation

$$k_{TOTAL} = 10^{12.28} \exp(-38{,}300/RT) \text{ Sec}^{-1}$$

By the use of Feick's equation (14)

$$P = 10^{8.502} \exp(-18{,}800/RT) \text{ cm Hg},$$

with the assumption that the total pressure in Cook and Abbeg's

---

A more recent reference for the rate of N_2O decomposition of ammonium nitrate can be found in the following work: Bennett, D.: J. Appl. Chem. Biotechnol. 22, 973 (1972).

experiments was 760 mm, their rate constants may be converted to those for the production of N_2O alone. The corrected rate constant is then

$$k_{N_2O/H_2O} = 10^{11.69} \exp(-37{,}000/RT) \text{ Sec}^{-1}$$

At 260°C, the rate constant for the dissociation reaction and N_2O decomposition becomes

$$k_{TOTAL} = 10^{12.28} \exp(-38{,}000/RT) \text{ Sec}^{-1}$$

$$= 10^{12.28} \exp(-38{,}300/1.987 \times 533^{\circ}K)$$

$$\log k_{TOTAL} = -3.44$$

$$k_{TOTAL} = 3.60 \times 10^{-4} \text{ Sec}^{-1}$$

and

$$k_{N_2O/H_2O} = 3.16 \times 10^{-4} \text{ Sec}^{-1}$$

Since the rate constant expresses the number of moles of ammonium nitrate decomposed, it can also indicate the number of moles of gas formed. For example, in the dissociation of ammonium nitrate into ammonia and nitric acid, each mole of ammonium nitrate yields 2 moles of gas. Similarly, in the decomposition to N_2O and H_2O, each mole of ammonium nitrate yields 3 moles of gas. Therefore, the number of moles of gas

produced at 260°C via reaction 1 is 2 x (3.60×10^{-4} - 3.16×10^{-4}), which equals 0.88×10^{-4} moles of gas (NH_3 and HNO_3). Similarly, reaction 2 yields 3 x 3.16×10^{-4}, which equals 9.48×10^{-4} moles of gas (N_2O and H_2O).

Therefore, the total number of moles of gas released in the decomposition of ammonium nitrate at 260°C are 10.36×10^{-4} Sec $^{-1}$.

From the ideal gas law, the volume occupied by these gases can be approximated as follows:

$$V = \frac{nRT}{P}$$

where V = volume of gas in litres

n = number of moles of gas

R = gas constant $\left(.082 \frac{\ell \text{ atm}}{^{\circ}K \text{ mole}}\right)$

T = temperature 533°K

P = ambient pressure (1 atmosphere)

$$V = \frac{10.36 \times 10^{-4} \times .082 \times 533}{1}$$

$= .0453 \ \ell$

$= 45.3 \ cm^3$

$= 45 \ cm^3$

Now, from extrapolated experimental data, ammonium nitrate has a density (quiescent) of 1.37 gms/cm^3 at 260°C.

Therefore, 1 mole of ammonium nitrate, which has a mass of 80 gms, occupied a volume of 58.45 cm^3.

However, 1 mole of ammonium nitrate has partially decomposed predominantly into NH_3, HNO_3, N_2O and H_2O, i.e. 3.60 x 10^{-4} x gms/mole = 0.029 gms of ammonium nitrate decomposing per second.

Thus the actual volume of fluid is 58.42 cm^3 which, when combined with a total gas release of 45 cm^3, yields a total volume of 103.72 cm^3. Since the total mass remains the same, i.e. 80 gms, the density resulting from aeration due to thermal decomposition and dissociation is .77 gms/cm^3, which agrees well with an experimentally determined density of .79 gms/cm^3 at the same temperature (260°C).

Liquid explosives can be exceedingly sensitive to impact, and the shock sensitivity of liquid explosives such as nitroglycerine is generally appreciated. For example Bowden and Yoffe (15) showed that a 40 gram cavity striker can initiate a drop of liquid nitroglycerine on an anvil by falling from a height of only 5 mm. Generally, they showed that air and gas inclusions in a rapidly compressed fluid give rise to hot spots in which combustion occurs, and a classic example of this is Winning's work on degassed nitroglycerine.

Ammonium nitrate in the liquid phase, especially at temperatures just above its melting point (169°C) is a clear to honey colored fluid which shows no visible tendency to decompose or dissociate as would be evidenced by release of gas bubbles.

As temperatures approach 210°C, however, decomposition becomes evident by production of gas bubbles. At 220°C gas evolution is quite pronounced and at 254°C to 260°C the liquid appears to "boil" quite violently. Clearly, then, the presence of gas bubbles is controlled by temperature, as should the sensitivity to external forms of stimuli such as shock, bullet impact, falling weights, etc...

Sensitivity, according to Cook (7) can be defined as the relative ease of causing an explosive to explode and a high explosive to detonate. It is not a particularly useful definition, however, because each type of sensitivity must be considered separately.

Some basic factors pertaining to sensitivity are known. Explosions rarely occur in most useful thermochemical type explosives until a critical temperature is reached, at which point the rate of chemical reaction may be considered "instantaneous". Critical explosion temperatures are sometimes listed in the literature to indicate to what temperature an explosive may be heated before it explodes. These temperatures are in fact however much

lower than the actual temperatures at which the explosion occurs. They are, however, the last measureable temperatures to which a self-accelerating thermal decomposition can be taken before the still relatively slow reactions can be attenuated by removing the heat source. Explosives generally require a short induction period after this indefinite "critical temperature" is reached. The explosion temperature, therefore, is not a fixed value at all, but depends on factors such as sample size, confinement, temperature gradients, thermal conductivities and rate of heating.

Four general types of stimuli are prominent in the precariousness of explosives: shock, heat, flame and electrical discharge. Each may cause a detonation to develop in high explosives if sufficiently intense. Shock implies supersonic actions such as high velocity impact, shock waves, etc...

All of these types of stimuli have been investigated extensively in solid ammonium nitrate.

One method of examining shock sensitivity for molten ammonium nitrate, which is a strong function of temperature, is by means of the critical primer weight test.

RESULTS

From the data plotted in Figure 25 it can be seen that the density changes due to thermal expansion are essentially linear up to ≈ 220°C, at which point the decrease in density due to "auto-aeration" as a result of thermal decomposition becomes significant. At temperatures > 250°C, the density decreases very quickly with each degree rise in temperature.

The results of the critical initiator tests, which are shown in Figure 26, show the dramatic increases in sensitivity as the temperature is raised 40°C from 200°C. In the test configuration used, it was not possible to initiate a stable detonation in the liquid phase system at temperatures less than 220°C even with a 1 lb primer. This would indicate a lack of a critical number of reaction centers necessary to promote detonation.

At temperatures greater than 240°C liquid phase ammonium nitrate can be initiated by electric blasting caps, and at 260°C it can be initiated to a state of detonation by a #6 cap, the smallest electric blasting cap made in this country, and, in fact, no longer in use. This puts liquid phase ammonium nitrate at 260°C on the same level of shock sensitivity as nitroglycerine based dynamites.

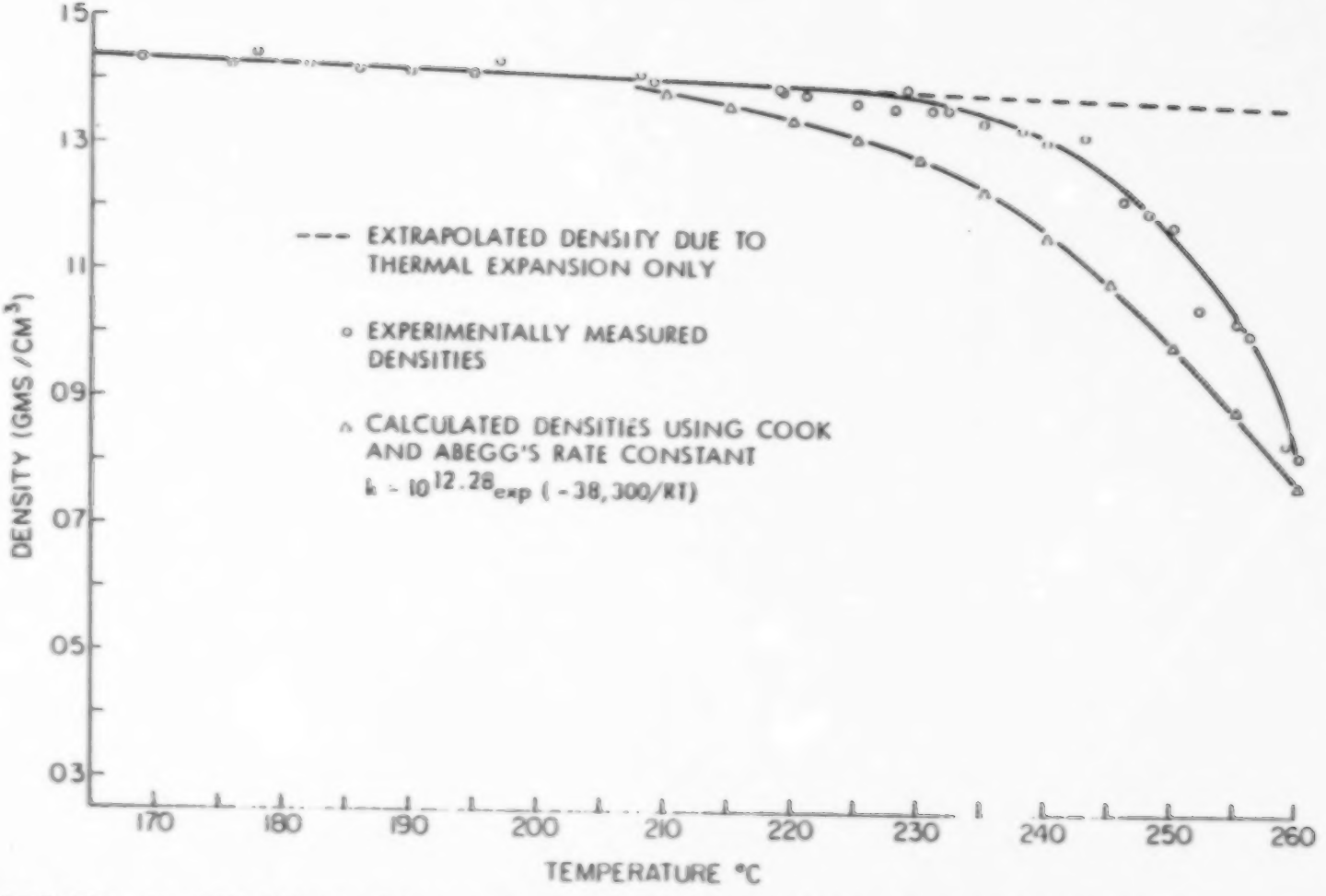


FIGURE 25 EXPERIMENTALLY DETERMINED DENSITIES AND CALCULATED DENSITIES FOR LIQUID PHASE AMMONIUM NITRATE FROM 170° C TO 260° C.

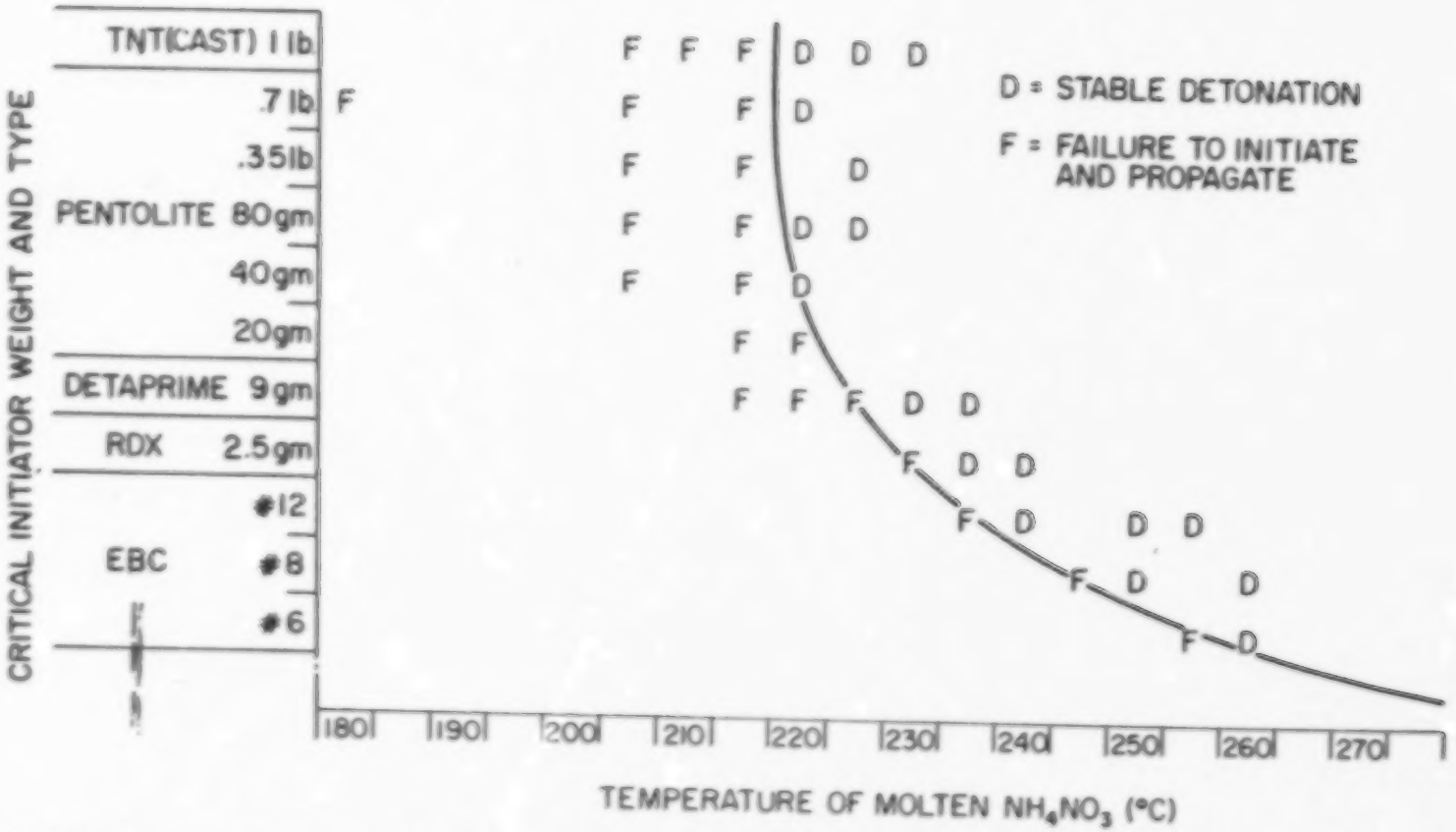


FIGURE 26 CRITICAL INITIATOR WEIGHTS AND TYPES FOR MOLTEN NH_4 NO_3 AS A FUNCTION OF TEMPERATURE.

In Figure 27 the relationship between charge diameter and the fraction of ammonium nitrate reacted in the detonation head is shown for two different temperature extremes, one at 220°C and one at 260°C. While the velocities in a given charge diameter are lower at higher temperatures due to the lower densities, the quantity of material reacting inside the detonation head is much greater.

Test charges much larger than 16 inches are very difficult to conduct due to the large amounts of power which are required to both melt the ammonium nitrate, and bring the test charge to final temperature, and would not give much more information than is available from 16 inch charges.

The sonic velocities in Figures 28 to 32 are indicated by C_o, and are given in meters per second.

A general relation of the velocity of detonation of molten ammonium nitrate as a function of temperature in 5" diameter steel canisters is shown in Figure 33.

The apparatus used to determine the velocities of detonation of molten AN as a function of temperature for large charges are shown in Figures 34 and 35.

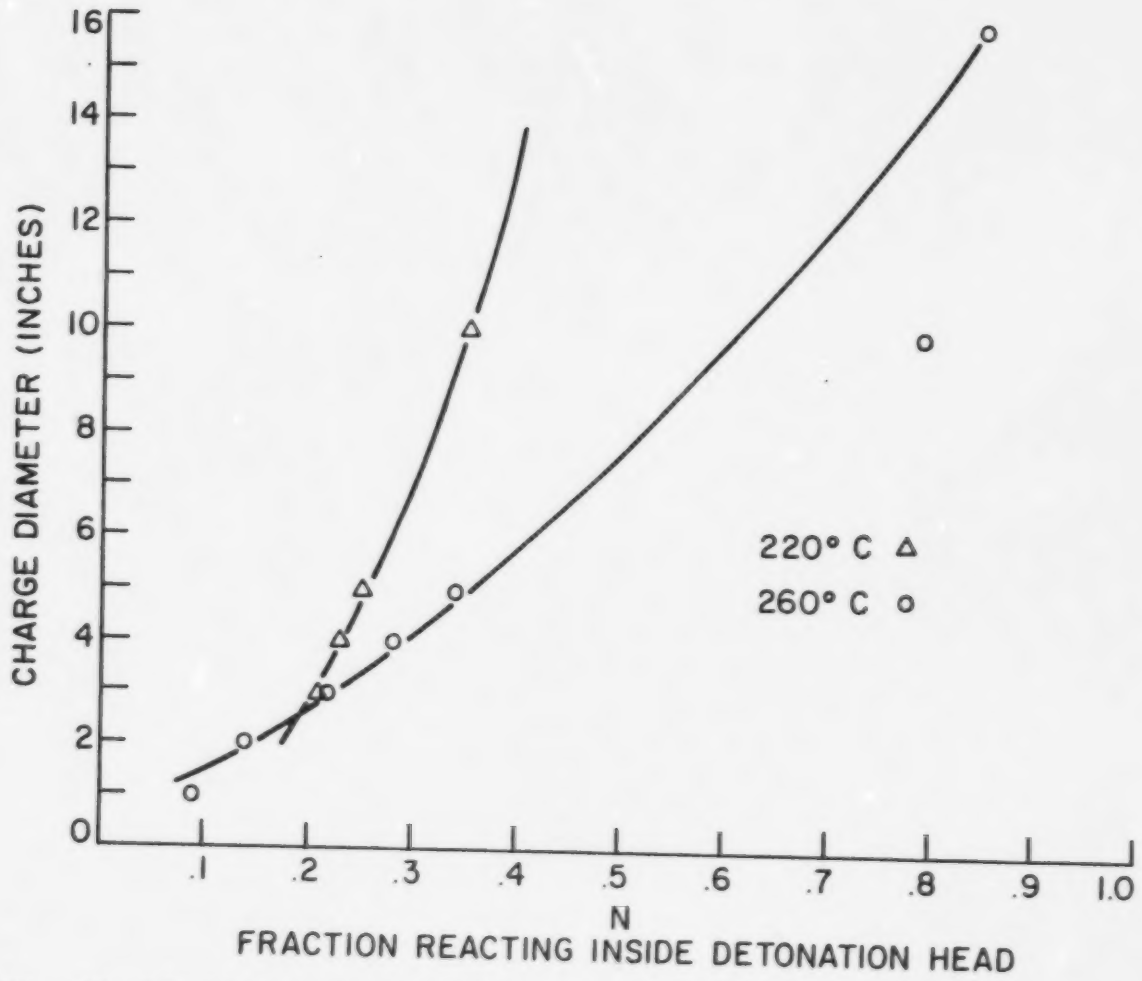


FIGURE 27 RELATIONSHIP BETWEEN CHARGE DIAMETER AND VOLUMETRIC FRACTION "N" REACTED INSIDE DETONATION HEAD FOR LIQUID PHASE AMMONIUM NITRATE AT 220° C AND 260° C.

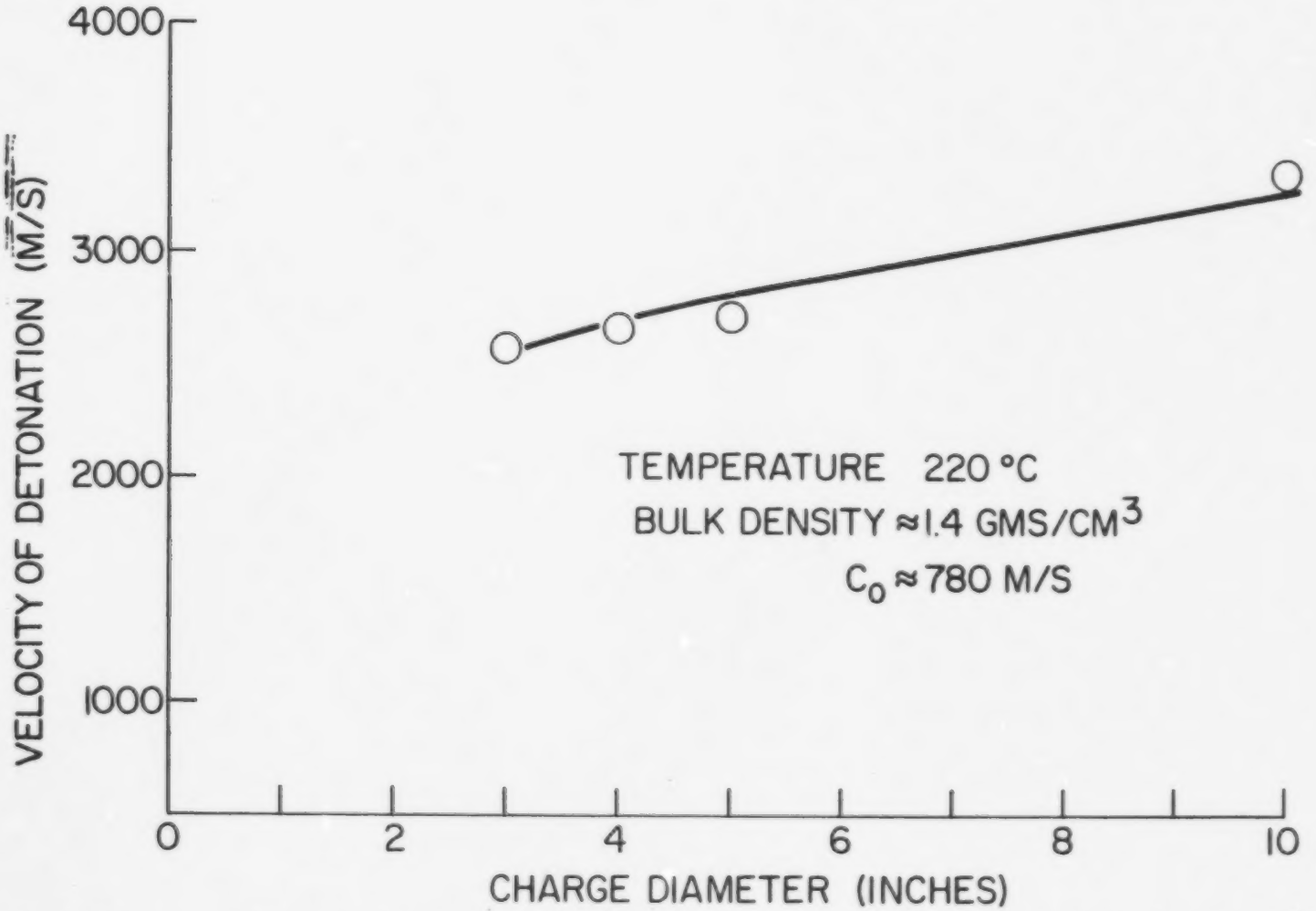


FIGURE 28 EXPERIMENTALLY DETERMINED VELOCITIES OF DETONATION AS A FUNCTION OF CHARGE DIAMETER UNDER HEAVY STEEL CONFINEMENT (1/2 INCH WALL) AT 220° C.

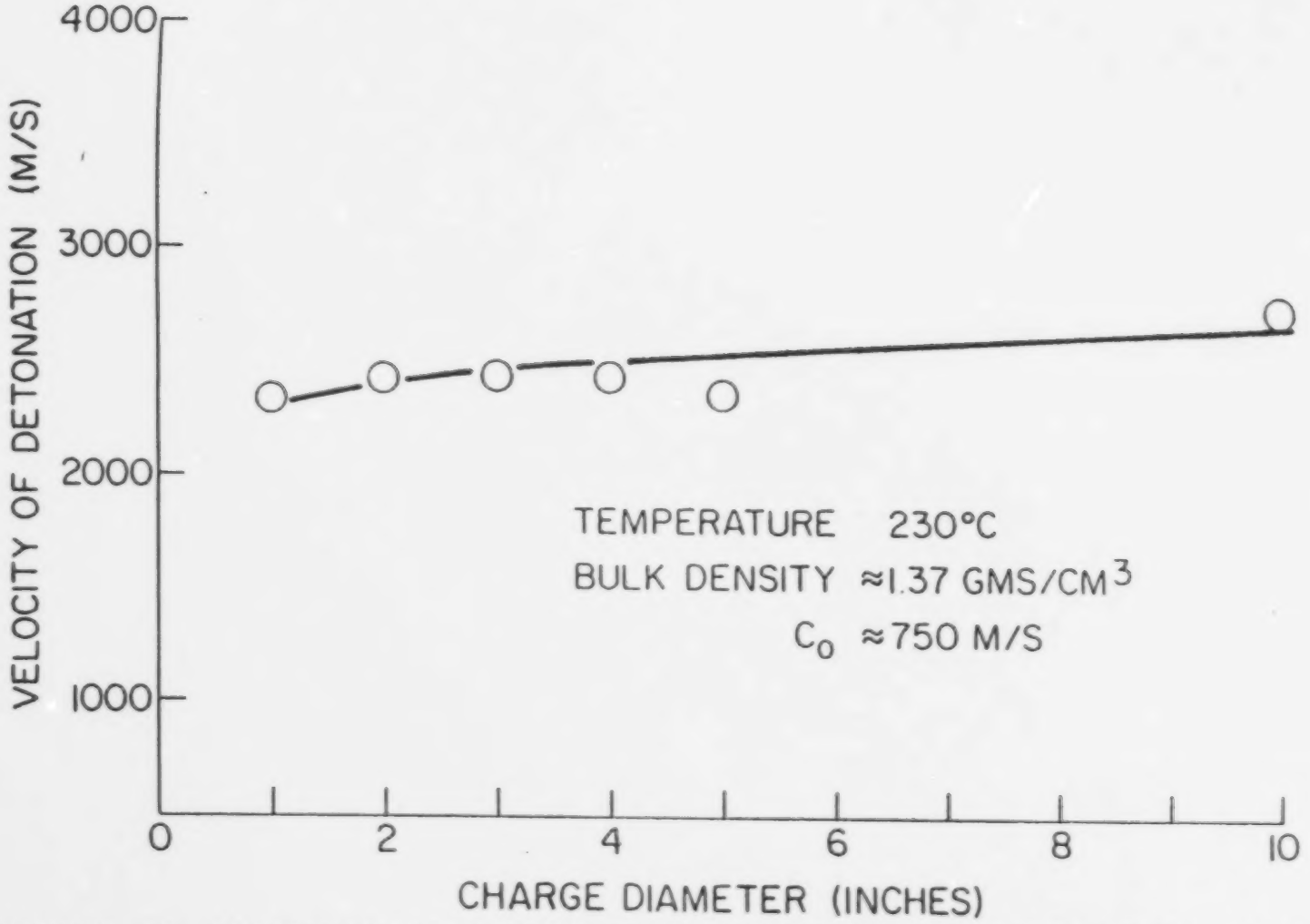


FIGURE 29. EXPERIMENTALLY DETERMINED VELOCITIES OF DETONATION AS A FUNCTION OF CHARGE DIAMETER UNDER HEAVY STEEL CONFINEMENT (1/2 INCH WALL) AT 230° C.

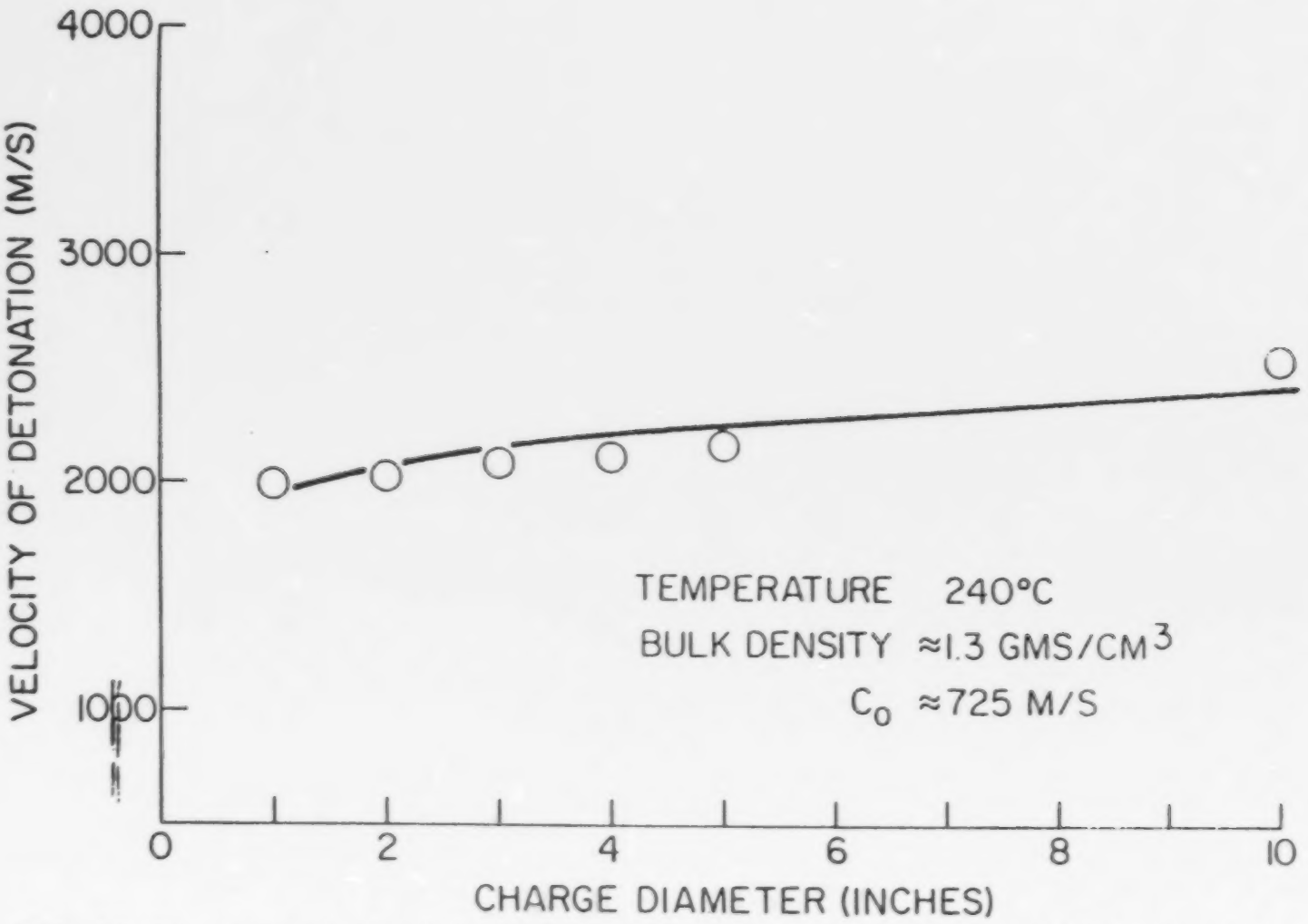


FIGURE 30: EXPERIMENTALLY DETERMINED VELOCITIES OF DETONATION AS A FUNCTION OF CHARGE DIAMETER UNDER HEAVY STEEL CONFINEMENT (1/2 INCH WALL) AT 240° C.

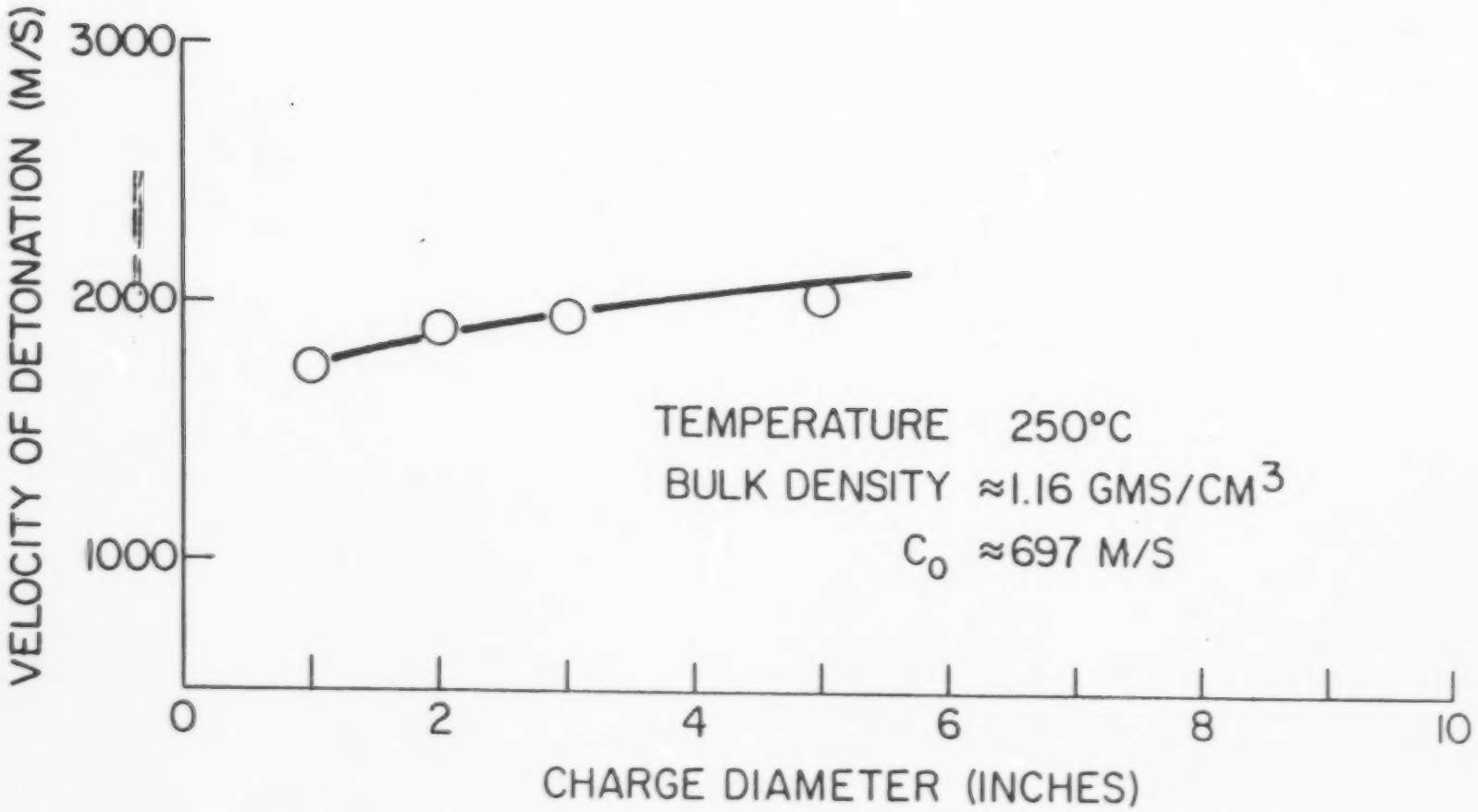


FIGURE 31: EXPERIMENTALLY DETERMINED VELOCITIES OF DETONATION AS A FUNCTION OF CHARGE DIAMETER UNDER HEAVY STEEL CONFINEMENT (1/2 INCH WALL) AT 250° C.

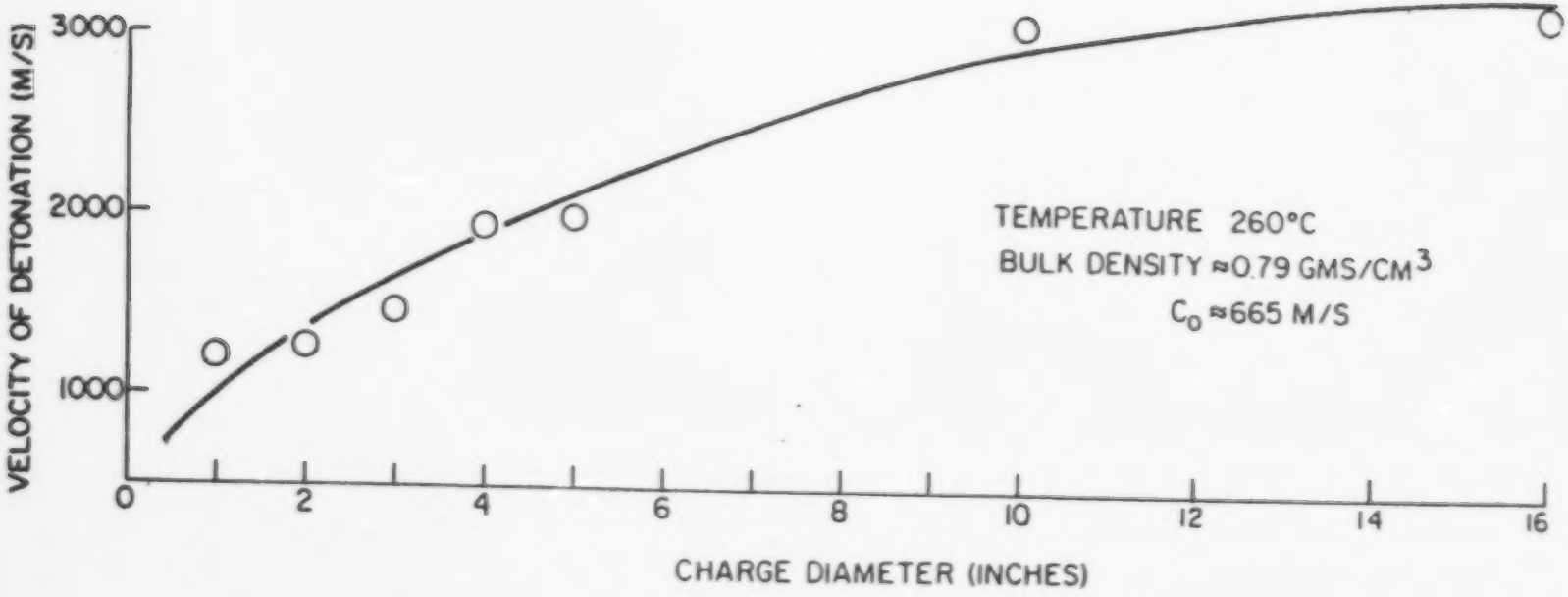


FIGURE 32: EXPERIMENTALLY DETERMINED VELOCITIES OF DETONATION AS A FUNCTION OF CHARGE DIAMETER UNDER HEAVY STEEL CONFINEMENT (1/2 INCH WALL) AT 260° C.

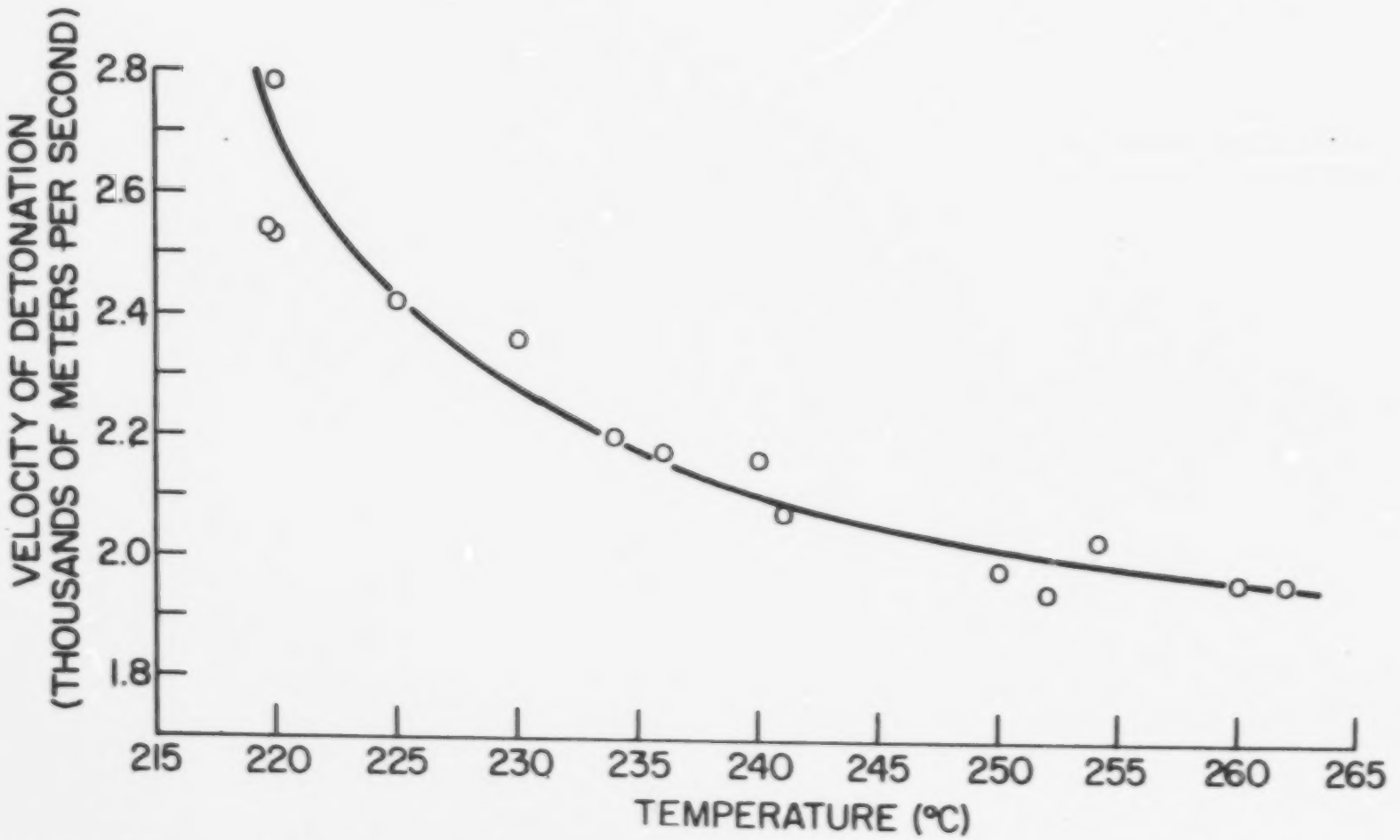
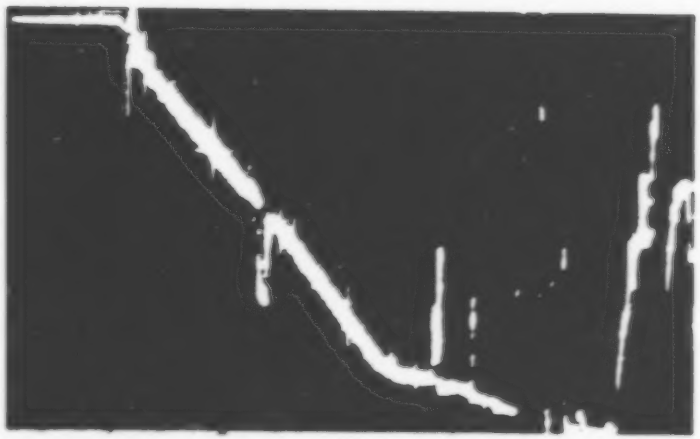


FIGURE 33 VELOCITY OF DETONATION OF MOLTEN AMMONIUM NITRATE AS A FUNCTION OF TEMPERATURE IN 5 INCH DIAMETER STEEL CANISTERS UNDER HEAVY CONFINEMENT (1/2" WALL).



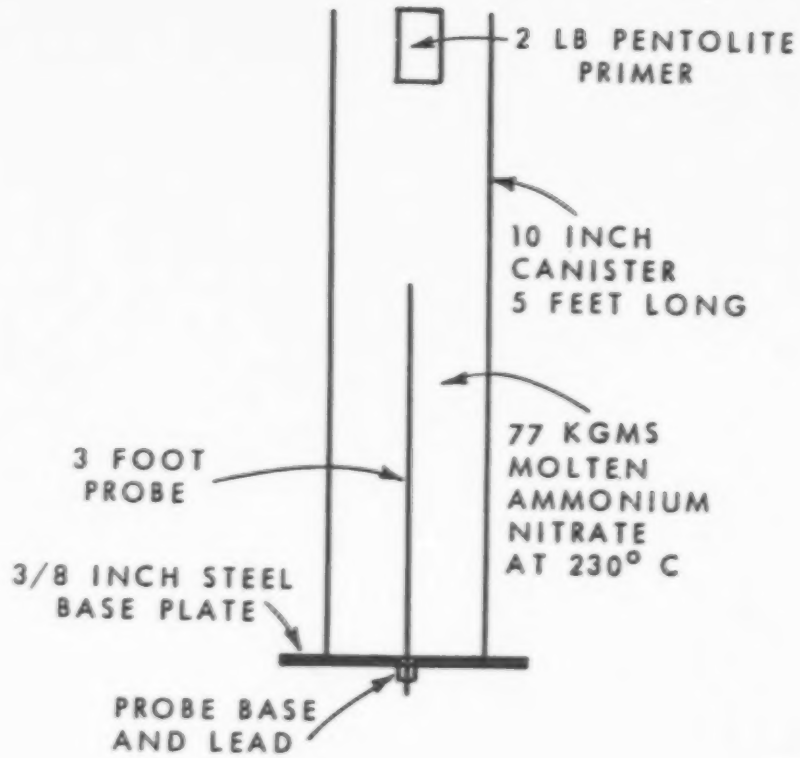
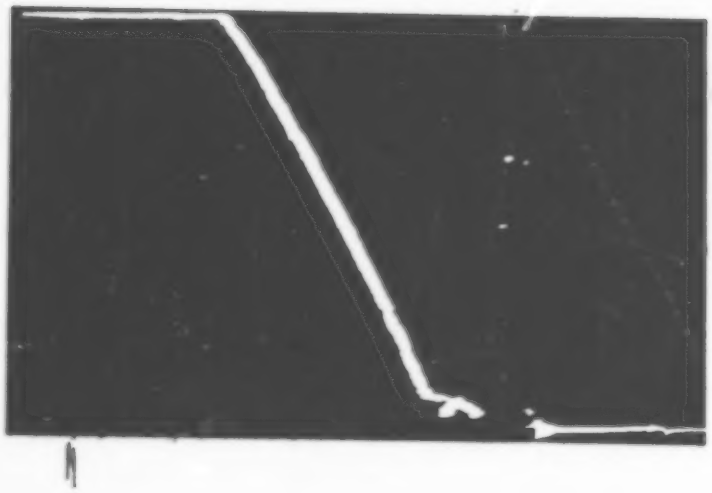


FIGURE 34 RELATIONSHIP BETWEEN THE OSCILLOSCOPE TRACE OF THE DETONATION PROCESS AND CHARGE GEOMETRY FOR A LARGE 10 INCH DIAMETER 60 INCH LONG MOLTEN AMMONIUM NITRATE SHOT AT 230° C.



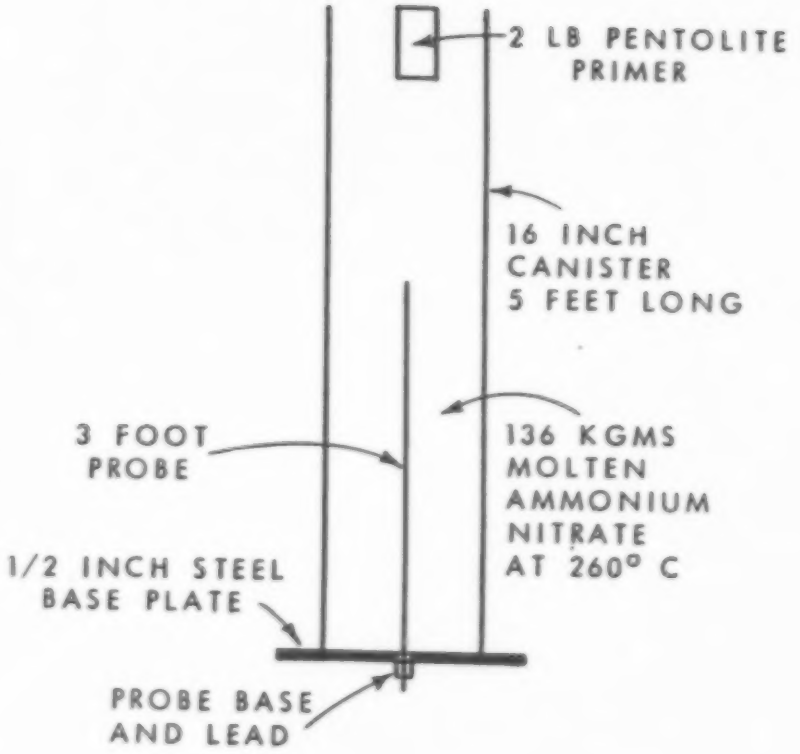


FIGURE 35 RELATIONSHIP BETWEEN THE OSCILLOSCOPE TRACE OF THE DETONATION PROCESS AND CHARGE GEOMETRY FOR A LARGE 16 INCH DIAMETER 60 INCH LONG MOLTEN AMMONIUM NITRATE SHOT AT 260° C.

DISCUSSION

The density of molten ammonium nitrate changes little as the temperature is raised from the melting point, at ≈ 170°C, to approximately 210°C. Over this temperature range, the density slowly decreases primarily as a result of thermal expansion only. At 210°C the evolution of N_2O and H_2O, as well as dissociation into NH_3 and HNO_3 becomes significant and at 220°C the liquid appears to be "boiling". The rapidity and violence of this boiling increases moderately up to 240°C. At 250°C the material is "boiling" at a very rapid but manageable rate, in that the material is not escaping from the vessel. At 254°C however, the character of the decomposition becomes erratic and the decomposing material ejects small quantities of molten material from the vessel and this trend continues with increasing violence up to 260°C. Throughout the range of decomposition temperatures studied the color of the decomposition products was predominantly white, which indicates that decomposition into NO_2 or NO did not occur. Also, the temperature of the decomposing ammonium nitrate began to drop as soon as the external source of heat was removed. This reflects the much greater endothermic nature of the volatization of ammonium nitrate into NH_3 and HNO_3 as opposed to the exothermic decomposition into N_2O and H_2O.

This very rapid decrease in density from 250°C to 260°C accounts for the increased shock sensitivity of the molten material, since many more reactive sites are now available for development and propagation of a reactive shock, i.e. detonation wave. Since very few bubbles, i.e. reaction sites, are apparent below 210°C, it follows that this material should be very insensitive to shock and have a very large critical diameter. This is in fact what is observed experimentally. It follows then that shock sensitivity and density should follow the same exponential change with temperature, although they are evidently not the same function of temperature. This is also observed experimentally.

From the data obtained in the region of 176°C to 209°C a regression analysis can be used to obtain an equation relating the density change as a function of temperature, which is essentially linear over this temperature range. This line can be extrapolated to 260°C which then gives the change in density resulting from thermal expansion over a wide temperature range, as shown in Figure 36.

From the slope of this line, the coefficient of volume expansion, B, may be calculated by means of the following expression for B :

$$B = \frac{1}{V}\left(\frac{\partial V}{\partial T}_{P}\right)$$

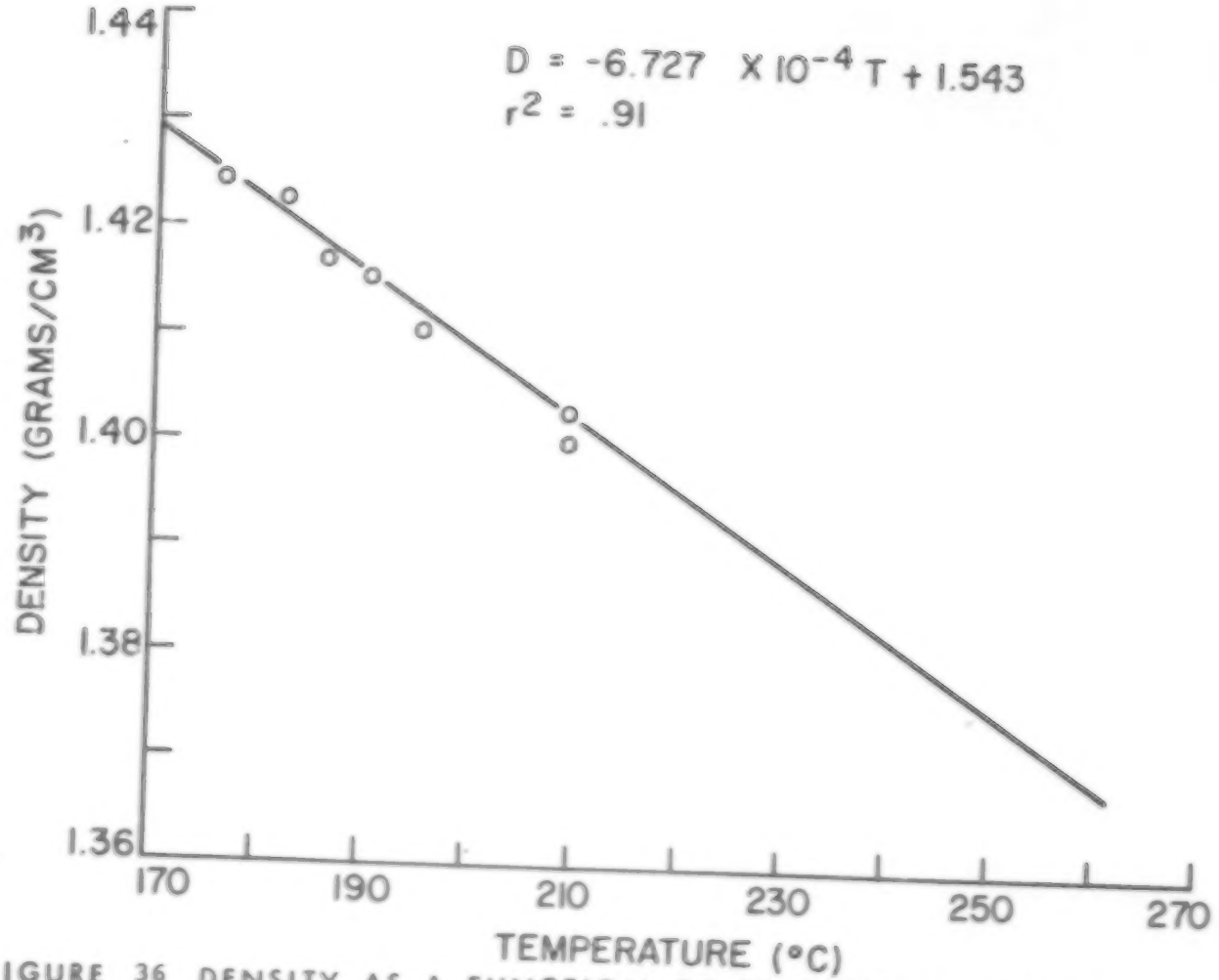


FIGURE 36 DENSITY AS A FUNCTION OF TEMPERATURE DUE TO THERMAL EXPANSION ONLY. DATA POINTS AND REGRESSION LINE ARE SHOWN.

From the velocity of detonation versus charge diameter curves it can be seen that the detonation velocity is a very slowly increasing function of charge diameter. The velocities of detonation recorded are all non-ideal when compared with the maximum theoretical velocities of detonation determined in Section 1, even up to charges of 10 inch diameter.

At 16 inches, only the 260°C test charge exhibited velocities approaching the maximum theoretical for that density. The behavior of liquid phase ammonium nitrate differs from that of other liquid explosives in that the velocities of detonation are not rapidly increasing function of charge diameter and do not rapidly approach the maximum theoretical velocity of detonation at that density as the diameter is increased. This may be partly explained by the relatively low temperatures of detonation and partly by the grain radius, and by the fact that at 220°C, the charge is only slightly above the dead packed state.

The grain radius, which is a function of bubble size and hence temperature, decreases as the temperature of the charge is increased. Therefore the extent of reaction in the detonation head will be greater than at the lower temperatures. This will not, however, be reflected in higher detonation velocities since the charge density decreases as the temperature increases. However, the velocities of detonation do appear to be increasing at a greater rate as the charge diameter is increased, relative to those measured at the lower temperatures.

CONCLUSIONS

The detonation characteristics of molten ammonium nitrate, like its shock initiation characteristics, are strong functions of density, hence temperature.

While this behavior is characteristic of all explosives, it is particularly important for explosives whose energy output or yield is relatively low. This is because significantly greater numbers of reactive sites become necessary to supply energy to propegate a reactive shock throughout the medium.

By examining the fraction of material reacted inside the detonation head, N, for two temperatures, and hence two different densities i.e. 220°C and 260°C, it becomes apparent that very large charge diameters are necessary to react even 50% of the material inside the detonation head at 220°C. This is also apparent in the very sluggish response of the velocity of detonation to changes in charge diameter.

Liquid explosives, in general, do not exhibit such behavior. Rather, they have very steep velocity of detonation vs charge diameter curves, and generally fail to detonate when N is less than ≈.92 - .96. This is especially true for explosives such as the Dithekite series (nitric acid-nitrobenzene-water) and nitromethane sensitized with ethylene diamine. Nitroglycerine also behaves similarly. Explosives of these types rely on compressed

From the velocity of detonation versus charge diameter curves it can be seen that the detonation velocity is a very slowly increasing function of charge diameter. The velocities of detonation recorded are all non-ideal when compared with the maximum theoretical velocities of detonation determined in Section 1, even up to charges of 10 inch diameter.

At 16 inches, only the 260°C test charge exhibited velocities approaching the maximum theoretical for that density. The behavior of liquid phase ammonium nitrate differs from that of other liquid explosives in that the velocities of detonation are not rapidly increasing function of charge diameter and do not rapidly approach the maximum theoretical velocity of detonation at that density as the diameter is increased. This may be partly explained by the relatively low temperatures of detonation and partly by the grain radius, and by the fact that at 220°C, the charge is only slightly above the dead packed state.

The grain radius, which is a function of bubble size and hence temperature, decreases as the temperature of the charge is increased. Therefore the extent of reaction in the detonation head will be greater than at the lower temperatures. This will not, however, be reflected in higher detonation velocities since the charge density decreases as the temperature increases. However, the velocities of detonation do appear to be increasing at a greater rate as the charge diameter is increased, relative to those measured at the lower temperatures.

CONCLUSIONS

The detonation characteristics of molten ammonium nitrate, like its shock initiation characteristics, are strong functions of density, hence temperature.

While this behavior is characteristic of all explosives, it is particularly important for explosives whose energy output or yield is relatively low. This is because significantly greater numbers of reactive sites become necessary to supply energy to propagate a reactive shock throughout the medium.

By examining the fraction of material reacted inside the detonation head, N, for two temperatures, and hence two different densities i.e. 220°C and 260°C, it becomes apparent that very large charge diameters are necessary to react even 50% of the material inside the detonation head at 220°C. This is also apparent in the very sluggish response of the velocity of detonation to changes in charge diameter.

Liquid explosives, in general, do not exhibit such behavior. Rather, they have very steep velocity of detonation vs charge diameter curves, and generally fail to detonate when N is less than $\simeq .92 - .96$. This is especially true for explosives such as the Dithekite series (nitric acid-nitrobenzene-water) and nitromethane sensitized with ethylene diamine. Nitroglycerine also behaves similarly. Explosives of these types rely on compressed

molecular hole volumes to initiate hot spots, the reaction expanding spherically outward from them and eventually coalescing into a reactive shock front. This is possible only because the energy output is very high, often exceeding 1000 calories per gram.

Explosives such as molten ammonium nitrate, whose energy release is 1/3 to 1/2 of this, rely on "macro" centers either artificially introduced into the fluid, or resulting from gaseous thermal decomposition products, to provide reaction centers. While molecular hole volumes are compressed in molten ammonium nitrate, the energy resulting from chemical reactions so induced is undoubtedly dissipated via conductive and endothermic processes before sufficient numbers of them can coalesce to form a reactive shock front.

The decrease in detonation velocity as temperature is increased (at a given charge diameter) reflects the decrease in bulk density. However, at high temperatures, the quantity of material reacted inside the detonation head is a maximum and at 260°C, the maximum theoretical velocity of detonation is approached in 16 inch diameter charges.

The detonation characteristics of molten ammonium nitrate differ somewhat from that of most liquid explosives, but in general, the characteristic velocity of detonation - charge diameter curves, critical diameter - minimum primer weight - density conform to that observed for most explosives.

5. DETONATION CHARACTERISTICS OF HIGH DENSITY PRILLED AMMONIUM NITRATE

INTRODUCTION

The detonation characteristics of ammonium nitrate and ammonium nitrate prills in particular have been rather thoroughly investigated in the past, especially since the disaster in Texas City in 1947.

There appears to be in the literature, however, a singular lack of information available concerning the detonation characteristics of high density ammonium nitrate, and the rather sluggish nature of detonating ammonium nitrate, has often led to much confusion as far as interpretation of such results are concerned.

One of the earliest works in that of Charles E. Munroe (16) which was prompted after the explosion in Oppau, Germany, in 1921 of a large pile of a double salt of ammonium nitrate-ammonium sulphate. In this work Munroe reviews the studies relating to the thermal decomposition of ammonium nitrate dating back to the mid 19th century, and up to the 1920's. Munroe also conducted tests for detonability on various types of ammonium nitrate (density unspecified) using boosters made from blasting gelatine. However, the quantities of ammonium nitrate tested were small

(400 grams up to 135 lbs) as were the boosters (25 grams up to 240 grams). Since the only method of evaluating a detonation was by means of the lead block compression test, no measure of the extent of detonation stability was obtained. Munroe concluded that "ammonium nitrate per se will propagate its own wave of detonation, but the force gradually falls off, as shown by the decrease in depth and width of the crater at the end opposite the priming charge". In light of the tests conducted at this department, such results would be considered to be a failure, and consequently cannot be classified as a detonation process.

More recently, and in particular since 1947, various investigations by industry and government have been carried out to determine under what conditions of heating and type of contamination will ammonium nitrate explode. These tests have, for the most part, also included a series of detonability tests.

A report by the Spencer Chemical Company (17) consisted of literature reviews and interpretations based on such reviews. A report issued by the U.S. Department of the Interior (Bureau of Mines) by Burns, Jones and Lewis (18) was a list of tests conducted on samples of the Texas City material. Closed bomb tests revealed that even with chemically pure ammonium nitrate, when heated under proper confinement explodes violently, with

fragmentation effects similar to that produced by the detonation of high explosives, and that the temperature at the time leading up to explosion was 277° to 334°C. None of the bombs ruptured or exploded when vent openings were larger than 1/8". There were, however, no tests conducted on the detonation characteristics of ammonium nitrate.

A similar report issued by Arthur D. Little, Inc. (19) in 1951 made an extensive investigation of the kinetics of the thermal decomposition but no tests were conducted on the detonation characteristics of the solid material.

The Advisory Committee on the Hazards of Ammonium Nitrate Transportation of the National Academy of Sciences - National Research Council, under contract with the U.S. Coast Guard, assembled a massive document called "A Compendium on the Hazards of Water Transportation and the Manufacture, Handling, Storage and Stowage of Ammonium Nitrate and Ammonium Nitrate Fertilizers". † This document dealt with the findings of most of the accidents to date involving ammonium nitrate, an extensive literature review of thermal decomposition tests and recommended practices in handling ammonium nitrate. There were, however, no tests conducted on the detonation characteristics of ammonium nitrate.

One of the first reports to examine the detonation characteristics of ammonium nitrate as a function of density was that

†Final report under contract no. TCG 38325 between U.S. Coast Guard and National Academy of Sciences Washington, D.C. December 15 (1953)

published by Fukuyama in 1957 (20). At densities of .5 to .7 grams/cm^3 Fukuyama obtained stable detonations under moderate confinement in a steel tube (2mm wall thickness), 12.5 mm in diameter with a #6 detonator.

In 1964 Winning and Fassnacht of E.I. DuPont de Nemours & Company (21) issued a report dealing with the detonation characteristics of prilled ammonium nitrate. These tests were the first large scale detonation tests to be conducted on ammonium nitrate prills of low and high densities. In these tests the prilled ammonium nitrate and its adjoining primer had a maximum weight of ≈800 lbs.

The primer used was a 98/2 prill oil mixture (.82 gms/cm^3) which was more sensitive than the prills but differed only moderately in energy, density and velocity. The primer was initiated with a disc of fine 70/30 amatol (1" thick) which was itself multiple point initiated with 50 gram pellets of RDX at the end of each "Primacord" line. The results are summarized below in Tables 4 and 5.

The results are somewhat inconclusive in that there appears to be vastly different critical diameters for materials of comparable densities. The primers utilized may have had some effect upon the results.

TABLE 4

PRILL PROPERTIES

Sample	A	B	C	D
Bulk Density (gms/cm^3)	.82	.81	.98	.88
Particle Density (gms/cm^3)	1.49	1.43	1.67	1.63
Screen Analysis, Tyler				
0 - 10 mesh	32%	56.0%	26.0%	49.0%
10 - 14 mesh	65%	39.0%	68.0%	45.0%
14 - 20 mesh	2.8%	4.5%	5.7%	5.8%
20 - 78 mesh	0.2%	0.5%	0.3%	0.2%
Moisture, %	0.1%	0.1%	0.5%	0.1%

TABLE · 5

CHARGE PARAMETERS AND DATA SUMMARY OF
AMMONIUM NITRATE PRILL TESTS

Charge Diameter (Inches)	Charge Length (Inches)	Initial Velocity/Distance 2700 m/s @ 25"	Terminal Velocity/Distance
Prill A 20	60	-	3200 m/s @ 51"
18	36	3100 m/s @ 14"	3000 m/s @ 27"
15¼	66	2700 m/a @ 25"	2750 m/s @ 51"
12 3/4	8?	2400 m/s @ 25"	850 m/s @ 75"
Prill B 20	50	-	2750 m/s @ 41"
15¼	56	2400 m/s @ 20"	1100 m/s @ 46"
Prill C 20	50	2900 m/s @ 15"	950 m/s @ 41"
Prill D 20	54	2150 m/s @ 19"	-

In 1966 the U.S. Bureau of Mines put together a very extensive report (RI #6773) titled, "Explosion Hazards of Ammonium Nitrate Under Fire Exposure" (Van Dolah, Mason, Perzak, Hay and Forshey) (4). In this report the sensitivity to explosives - derived shocks of various types of ammonium nitrate prills was investigated by means of a card-gap test. In order to better determine the relationship between critical diameter, confinement and temperature for ammonium nitrate prills a series of charges of various diameters from 1 1/2 to 12 inches were fired using pressed Tetryl boosters, the weight of Tetryl being scaled with the diameter of the charge. For charges larger than three inches, composite boosters were formed by clustering pellets on the face of the charge and initiating these simultaneously by a single centered booster.

The results of these trials are shown in Tables 6 and 7.

While this data relates the number of initiations (as a function of booster size, charge diameter and confinement) to temperature, there is still no indication that these initiations were propagated at a constant rate throughout the length of the charge.

The data from tests conducted over the years would thus tend to indicate that, due to the insensitivity of ammonium nitrate, its rate of detonation and susceptibility to initiation by shocks

TABLE 6

SHOCK SENSITIVITY AND DETONATION RATE OF AMMONIUM NITRATE PRILLS AS A FUNCTION OF TEMPERATURE

Charge Diameter - 1 1/2" Schedule 40 Seamless Steel Pipe (1.61" F.D. x 0.145" wall)

Charge Length - 16"

Booster Type and Configuration - 160 gram pressed Tetryl (2" diameter x 2" length, ρ_o = 1.57 grams/cm^3)

Attenuator - Cellulose Acetate Waters

Procedure - 5 trials at each temperature; where detonation is observed, a 50% gap value is determined with 20 trials.

Prill Type	Density(gms/cm^3)	20°C	100°C	120°C	140°C
A	0.79	0/5	0/5	0/5	(2) 3/5
E	.81	0/5	0/5	(3)	(4)
G	.98	0/5	0/5	0/5	(5) 3/5
H	.79	0/5	0/5	0/5	1/5

Zero gap unless otherwise indicated

(2) Average Rate for 3 trials, 1900 m/s

(3) Average Rate for 5 trials, 2020 m/s 50% value 0.16" gap

(4) Average Rate for 5 trials, 2040 m/s 50% value, 1.16" gap

(5) Average Rate for 3 trials, 1,960 m/s

TABLE 7

THE EFFECT OF TEMPERATURE ON THE DETONABILITY OF PRILLED AMMONIUM NITRATE AT DIFFERENT DIAMETERS IN A 24-INCH CHARGE[5].

(Number of initiations (In.) per number of trials indicated by 3/5, etc., where 5 trials gave 3 initiations)

	Heavy confinement,[1] diameter and booster weight								Light confinement,[2] diameter and booster weight									
	1½ inch, 160 g		2 ½ inch, 360 g		4 inch, 320 g		6 inch, 640 g		3 inch, 360 g		4 inch, 320 g		6 inch, 640 g		8 inch, 1,280 g		12 inch, 1,440 g	
	°C	In.	°C	In.	°C	In.	°C	In.	°C	In.	°C	In.	°C	In.	°C	In.	°C	In.
Brand A prills:																		
Test 1	140	3/5	90	2/2	71	1/1	21	1/1	140	0/2	140	1/5	[3]75	1/1	45	1/1	20	1/1
Test 2	120	0/5	80	1/1	50	1/1	-	-	120	0/1	130	0/1	[3]65	1/1	35	1/1	-	-
Test 3	100	0/5	75	1/2	40	1/1	-	-	-	-	90	0/1	[3]54	1/1	-	-	-	-
Test 4	-	-	-	-	34	0/1	-	-	-	-	84	0/1	[3]45	0/1	-	-	-	-
Test 5	-	-	-	-	-	-	-	-	-	-	75	0/1	-	-	-	-	-	-
Brand E prills:																		
Test 1	140	5/5	70	1/1	35	1/1	20	1/1	140	0/2	130	1/1	50	1/1	30	1/1	20	1/1
Test 2	120	5/5	66	0/1	28	0/1	-	-	120	0/1	125	1/3	40	1/1	26	1/1	-	-
Test 3	100	0/5	65	0/1	-	-	-	-	-	-	120	0/1	35	0/1	22	0/1	-	-
Test 4	-	-	65	0/1	-	-	-	-	-	-	80	0/1	30	0/1	21	0/1	-	-
Test 5	-	-	-	-	-	-	-	-	-	-	74	0/1	-	-	-	-	-	-
Test 6	-	-	-	-	-	-	-	-	-	-	65	0/1	-	-	-	-	-	-

[1] Schedule 40 steel pipe.

[2] 24- to 28-gage stove pipe except as indicated by footnote 3.

[3] 1/4-inch-wall cardboard tube.

are strongly dependent upon particle size, apparent density, degree of confinement, efficiency of primer charge and temperature of charge. An increase in detonation rate is brought about by a decrease in particle size, decrease in apparent density of charge and increase in confinement.

The behavior of large masses of ammonium nitrate prills, however, whether low of high density, may be quite different from that of small cylindrical charges with minimum primers, when viewed from the ability of such masses to sustain stable detonations. In other words, while the same prill may fail to propagate a stable detonation in an 8" or 24" diameter cylinder when primed with 5 lbs of TNT for example, it may detonate completely when assembled in piles which more closely approximate bulk storage dimensions commonly encountered in industry today because of the diameter effect.

Since the size of bulk storage piles of ammonium nitrate prills commonly encountered in Canada vary from 8000 tons to over 30,000 tons in conical loading piles, and since the actual quantity amassed in bulk storage operations can approach 50,000 tons due to the cyclical nature of the requirements of the fertilizer industry, the detonation characteristics of large masses of ammonium nitrate prills should be studied.

Further, since the bulk of large storage operations consists of the high density material (ρ_o>.87 gms/cm^3), about which the detonation properties are little understood, greater attention should be given to this type of material in any test series.

Consequently, the test series started out with a 400 lb. test charge of roughly cylindrical geometry ≅24-27 inches in diameter primed with a 5 lb. TNT primer. The materials tested represented a broad range of prill types and densities.

Further testing on hemispherical piles (3' radius) of approximately 1 ton size were also conducted on an extensive range of Canadian manufactured ammonium nitrate prills.

Finally, testing on hemispherical piles (6' radius) of approximately 8 ton size were conducted on high density prills exclusively (ρ_o >.9 gms/cm^3).

RESULTS

Critical Diameter - Minimum Booster Weight Relationships

Generally, the larger the critical diameter, the greater the minimum booster weight required to initiate a stable detonation. This reflects the longer reaction time in the detonation head of high density materials (hence large detonation heads) and is especially true for mechanically mixed oxidizer-fuel systems, such as ANFO. This is shown in Figure 37.

The same relation can be shown to hold true for ammonium nitrate at varying densities, regardless of whether or not the state of the material is liquid or solid.

Charge Diameter - Density Relationships and the Significance Of Hemispherical Geometry in Large Scale Detonations

From the data available in the literature (4), and testing done to date (23), the graph illustrated in Figure 38 below was compiled. This figure shows the relationship between charge diameter and density, as well as the associated detonation-failure regimes. At densities of .9 grams/cm^3 or greater, ammonium nitrate prills, especially those of the type used in agriculture, are quite insensitive to initiation, thereby requiring large diameter charges and heavy boostering. From the

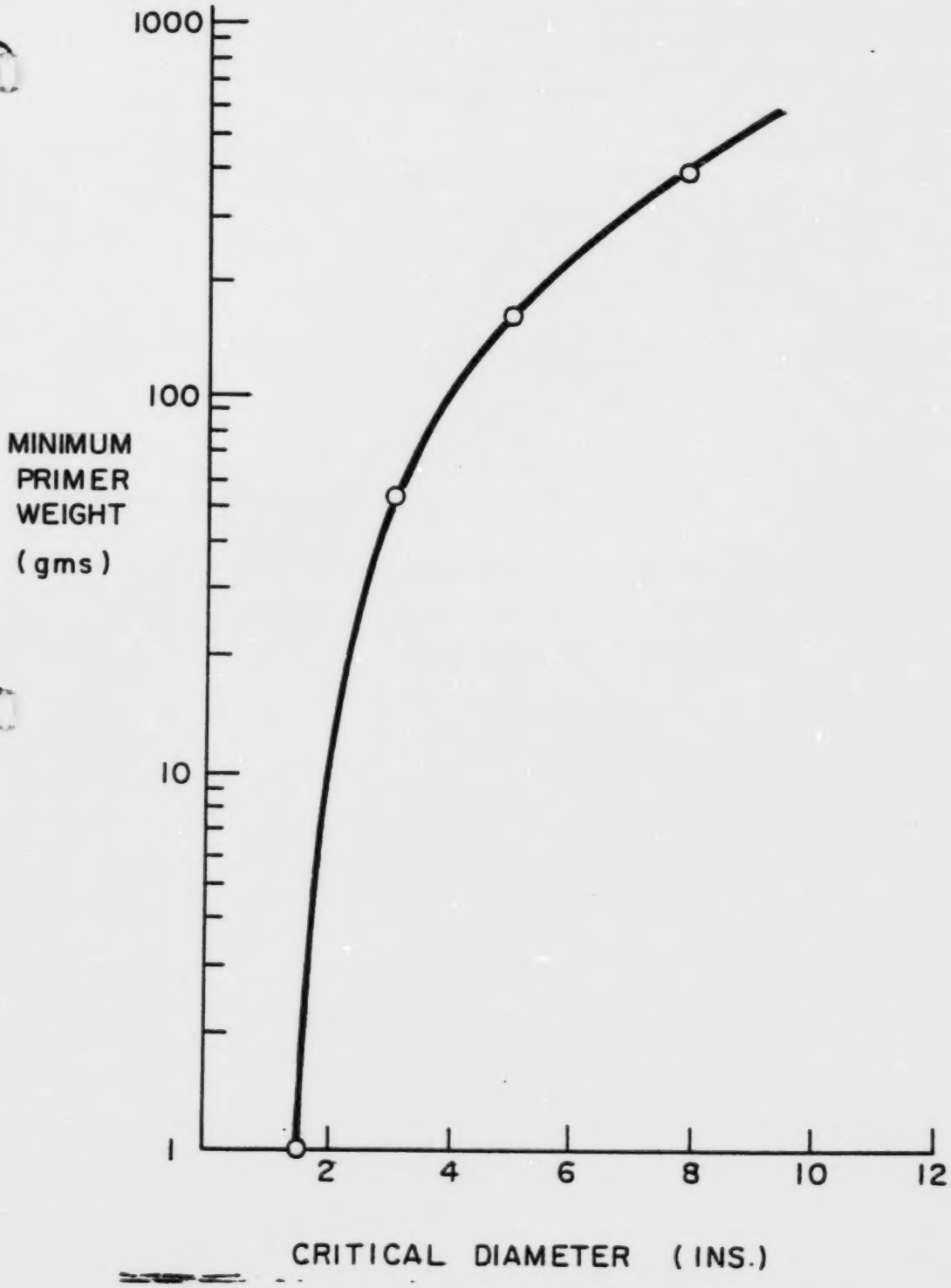


FIGURE 37 MINIMUM BOOSTER WEIGHTS FOR PRILLED AMMONIUM NITRATE/FUEL OIL AS A FUNCTION OF DIAMETER.

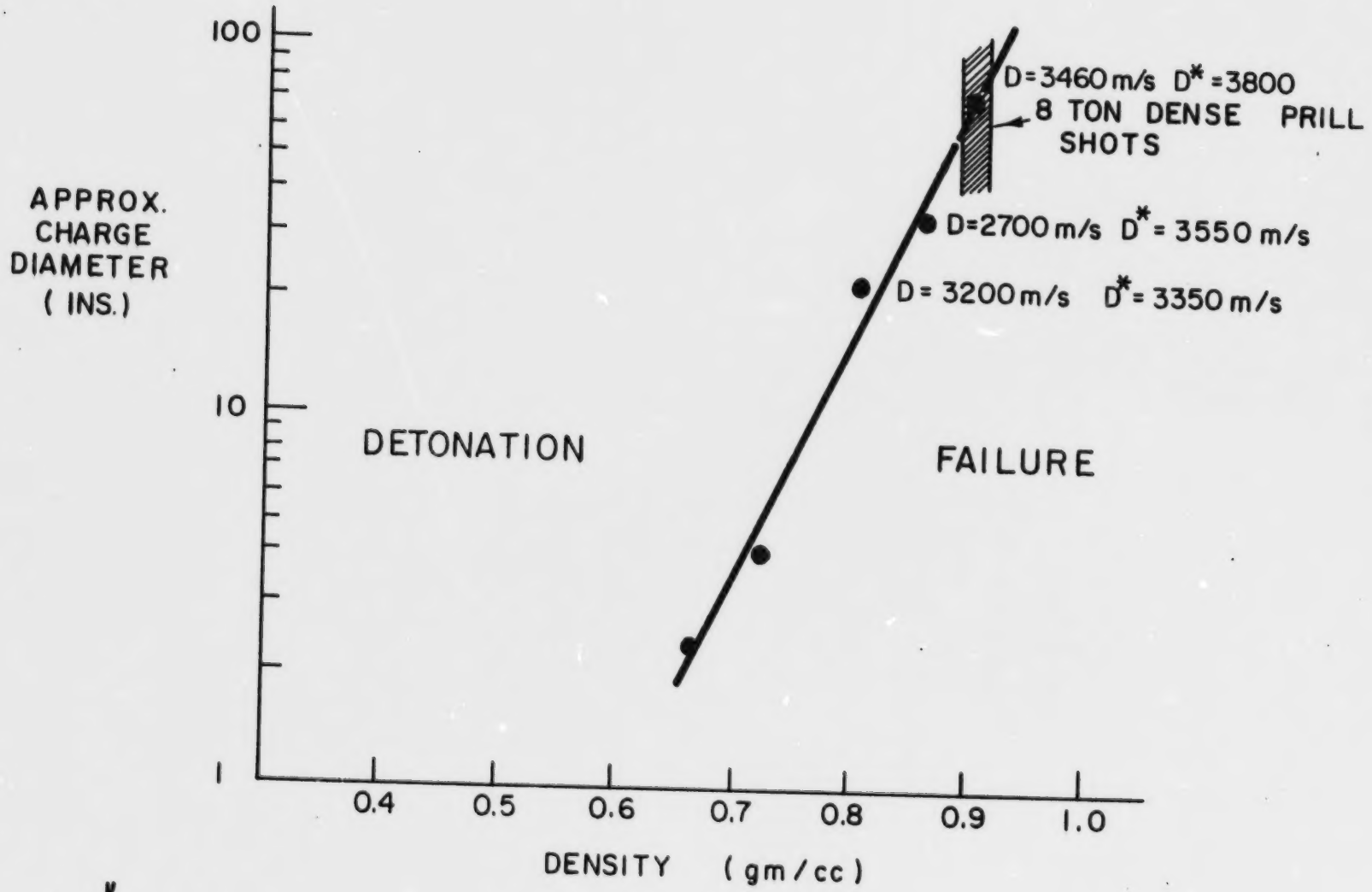


FIGURE 38: CRITICAL DIAMETER AS A FUNCTION OF DENSITY FOR VARIOUS AMMONIUM NITRATE PRILLS.

graph it can be seen that charge diameters of the order of thirty to forty inches may be required, and charge lengths of approximately three to four charge diameters are also necessary to allow the detonation head to reach its maximum stable velocity. Aside from the difficulty in assembling such a large Charge, D* is approached much more slowly due to massive rarefaction effects in cylindrical geometry. Also, a very large primer such as would be necessary to initiate such a mass, would occupy a very small fraction of the exposed surface area. Assuming end initiation to be the mode, there is some question as to just how much energy actually goes into initiating the mass of prills. Clearly, large cylindrical charges can introduce complicating effects, especially when very insensitive materials are studied. Also, the behavior of very insensitive materials when examined in this manner, may again behave quite differently in a large bulk storage pile, which in itself is more closely approximated by large test charges of hemispherical configuration.

Ideally, however, the size of head necessary to achieve D should be the same in both configurations.

The detonation head model of Cook (24) has been applied to detonation in liquid explosives when arranged in a cylindrical configuration. Hemispherical charges differ from cylindrical

geometry in that the detonation wave is almost perfectly confined and a significant negative particle velocity is unlikely. Also, the detonation head is not of one size determined by charge geometry at the outset of initiation, but rather is constantly increasing until finally it attains the size of the hemisphere or sphere itself.

According to Cook (24) the detonation wave is followed by a rarefaction wave (velocity ≅5/8 D) which forms the rear boundary of the detonation head. Therefore, by studying the initiation and growth of detonation in a hemispherical or spherical pile the actual thickness of that reaction zone which is necessary to achieve maximum theoretical velocity of detonation can be determined, provided the pile itself is large enough.

Furthermore, the actual distance between the two fronts, and hence the actual thickness of the detonation head can be calculated for any time, provided that the time chosen does not exceed that required to consume the pile. The thickness of the detonation head thus determined cannot be less than that calculated at the outset of initiation.

Therefore, if the thickness of the head necessary to establish the maximum theoretical velocity of detonation, D*, is, for example, ≅ 1 meter, and if a stable detonation cannot be sustained

at any velocity D $\leq .6D^*$, detonation failure will occur for any spherical or hemispherical charge of radius $\leq$ 1 meter, provided the critical booster weight requirements are met.

Effects of Bulk Density on the Detonation Characteristics of Liquid and Solid Ammonium Nitrate

The reaction process in solid and liquified ammonium nitrate in reality differs little. In the solid material, as shown earlier, the reaction process is essentially a burning inward phenomena, whereas in liquid explosives, the reaction process is a burning outward phenomena. In liquified ammonium nitrate for example, gas bubbles are formed by the decomposition reactions at elevated temperatures, and these gaseous decomposition products can form reaction sites. When the bubbles are rapidly compressed, as for example when a detonation front impinges upon them, they are very rapidly compressed and become heated "adiabatically", to temperatures far in excess of that necessary to decompose the explosive surrounding them. This then results in a burning outward process. The grain radius, then, becomes the distance from the center of the hot spot to the perimeter of a region where another hot spot has burnt out to, such that the distances from the centers of the respective hot spots to the outer perimeters of their reacted regions are equivalent. At this point the bulk of the liquid is consumed, and if the grain radius is such that the bulk of the fluid is consumed before leaving the detonation head, detonation is said to be ideal. This is shown in Figure 39.

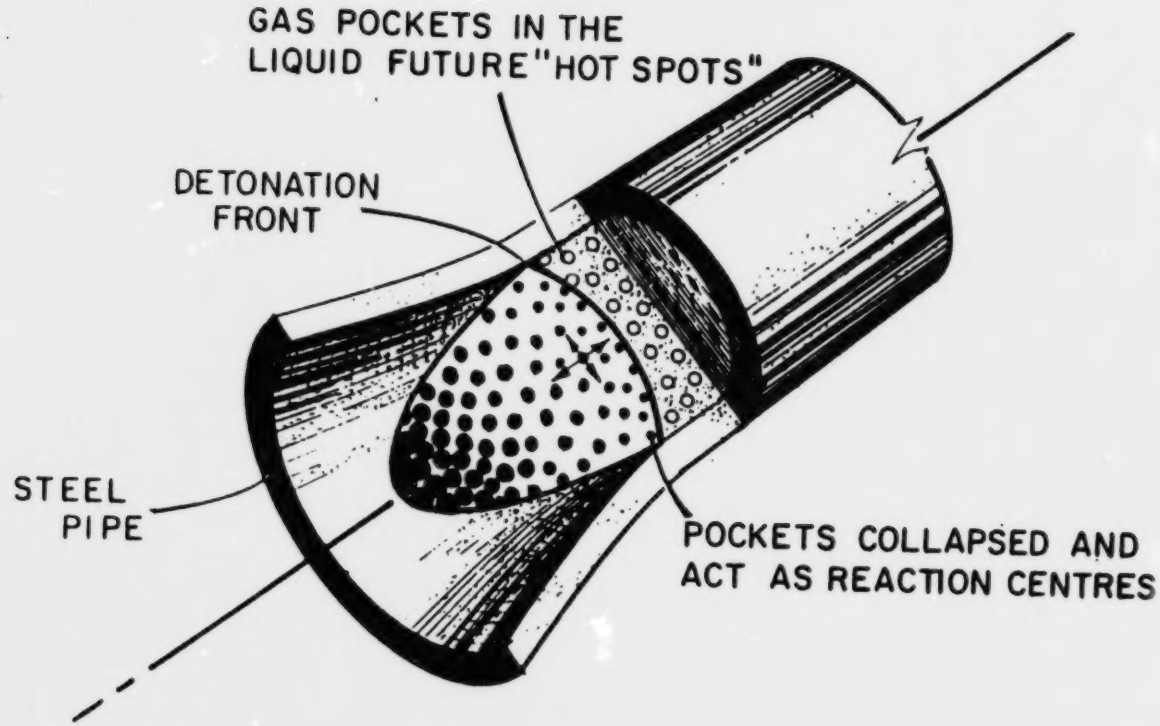


FIGURE 3: DETONATION PROCESS IN A LIQUID EXPLOSIVE ASSEMBLED IN CYLINDRICAL GEOMETRY.

The ideal velocities of detonation recorded in both systems should be equivalent, provided the charges are at the same density. The critical diameters, however, can be vastly different since: the rates of material consumed at a given linear burning rate are different; in inverse burning the products are trapped within the flame front; liquids are much better shock transmitters than porous solids, and since the liquid is several hundred degrees hotter than the solid. These two effects combine to increase the reaction rate to a much greater extent than in solids.

It is possible, however, for liquid explosives to exhibit the same dead-packing effects as solids. An insufficient number of gas bubbles in liquids, or annular spaces or micropockets in solids, have the same effect, i.e. to cut down on the number of available reactive sites, thereby reducing the energy available to the detonation front for propagation to a level where detonation failure occurs. This is shown in Figure 40.

It should be pointed out, however, that molten ammonium nitrate at a bulk density of 1.4 grams/cm^3 (220°C) is quite detonable, whereas solid ammonium nitrate at the same bulk density is quite inert, and has a very large critical diameter.

In a low energy system such as high density ammonium nitrate where the energy release is only 300 - 400 calories per gram the importance of providing an adequate number of reactive sites becomes even more important. Even slight increases in bulk density from 0.8 to 0.9 grams/cm^3 have a large effect in increasing both the critical diameter and critical booster weights, thereby necessitating very large charges to study the detonation characteristics of these high density systems.

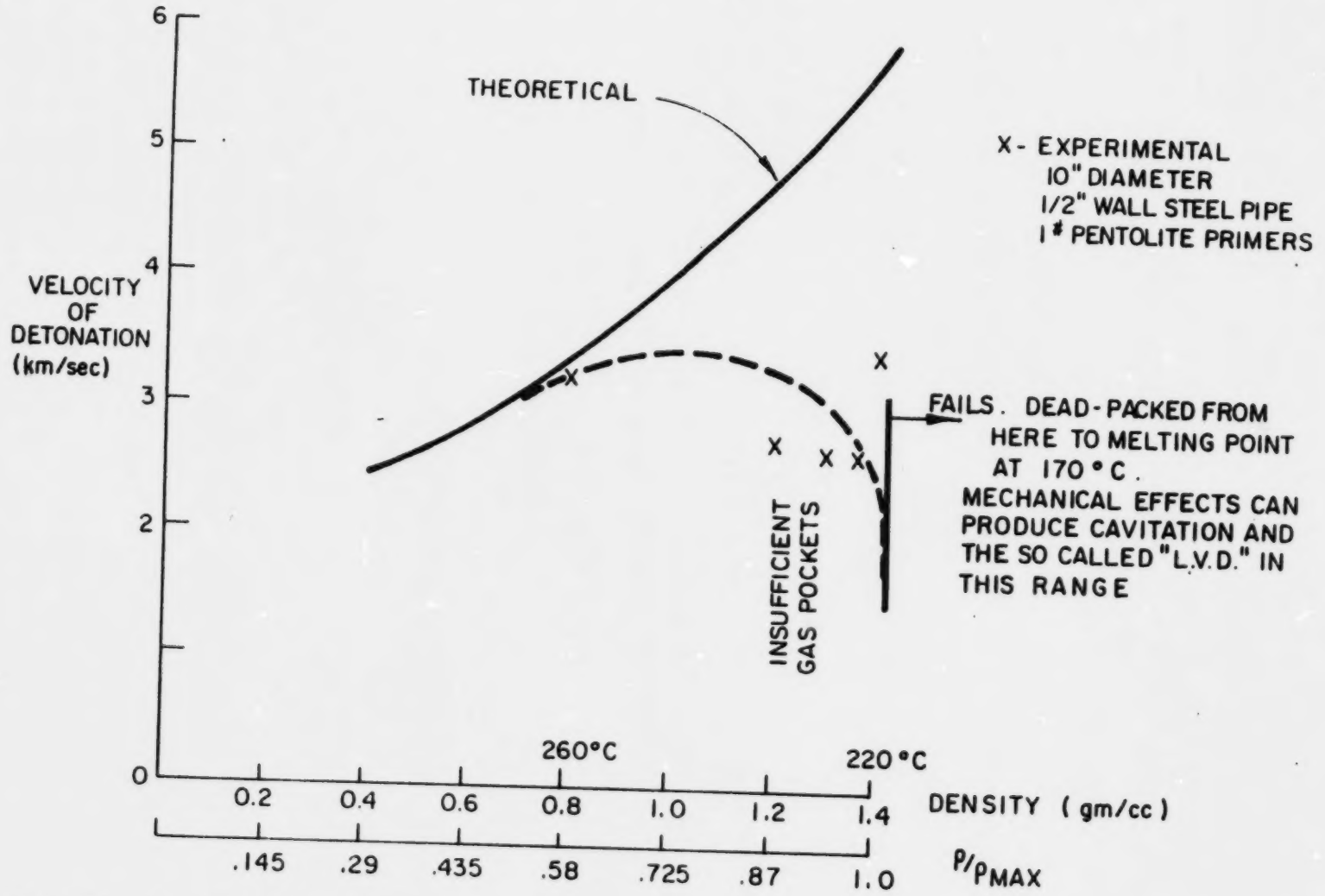


FIGURE 40 THEORETICAL AND MEASURED VALUES FOR THE DETONATION OF MOLTEN AMMONIUM NITRATE PLOTTED AS A FUNCTION OF DENSITY.

EXPERIMENTAL TESTS ON LOW AND HIGH DENSITY PRILLS

400 lb. Test Series

These tests were conducted on prills in a cylindrical geometry (diameter 22 inches, length 34 inches). All tests were instrumented for velocity of detonation with continuous velocity probes, and all were initiated with 5 lb Procore TNT primers. The purpose of these tests was to study detonation stability and velocity transients to achieve stable velocities. The following prill types were tested:

CIL Low density (ρ_o = .78 gms/cm^3)
Genstar Low density (ρ_o = ,78 gms/cm^3)
Cyanamid High Density (ρ_o = .86 gms/cm^3)

With the exception of CIL's low density prills, all exibited curved traces indicative of a fading detonation. While Genstar's 2% coated prills have a density comparable to that of CIL's prills, the heavy clay coating evidently has a strong effect on suppressing the detonation front, and this tendency was evident in the 4 inch pipe tests as well(23).

The results were a marked change from the 4 inch pipe tests, where both Genstar's material and that of Cyanamid's as well, failed to achieve a stable detonation. The results indicate that given a sufficiently large diameter with adequate boostering, it may be possible to initiate a stable detonation in those prills which failed in the 4 inch diameter tube test.

The data for these trials is summarized below in Table 8.

TABLE 8

400 lb. TEST SERIES DATA SUMMARY

Charge Diameter (inches)	Charge Length (inches)	Prill type	Density Grams/cm^3	V.O.D. Meters/Sec
22	34	CIL	.78 - .80	3110
22	34	Genstar	.78	F*
22	34	Cyanamid	.86	F*

*Curved Traces indicating velocity instability

2000 Lb Test Series

a) CIL Low Density Prills

These charges were assembled in a roughly hemispherical configuration with a radius of approximately 3 feet. The charges were centrally initiated with 97 lbs of Pentolite and the velocity of detonation was monitored with 3' long continuous velocity probes.

All trials were photographed with 16mm film at 15.6 milliseconds between frames on High Speed Ektachrome film (Type 7241), and with 35mm film as well.

When the 16mm film is examined frame by frame, it can be seen that little or no unreacted prills are being ejected from the pile.

From the constant velocity trace a velocity of detonation of 3290 meters/second was recorded, which, at that density of 0.80 grms/cm^3, represents a velocity of almost 97% of that of D (3400 meters/second).

b) Genstar XP Prills

Upon examining selected 16mm frames, no discernible quantity of unreacted prills could be seen being ejected from the exploding pile.

The oscilloscope trace indicated that the detonation front was propagating through the pile at a velocity of 3200 meters/second, which is 98.5% of that of D * (3250 meters/second) at that density of .74 grams/cm^3.

c) The Cyanamid Prills

Cyanamids low, medium and high density prills were tested in a similar manner. Selected 16mm frames of the detonation process are shown

in Figure 41 for the low density material; Figure 42 for the medium density material and Figure 43 for the high density material. Only in Figure 42 and 43 can significant quantities of ejected prills be seen. The corresponding constant velocity traces are shown in Figures 44 to 46 and summarized as follows:

Cyanamid Low Density (C-3) Prills - D = 3210 m/s

Cyanamid Medium Density Prills - D = 2670 m/s

Cyanamid High Density Prills - D = Failure

The velocities recorded are 94.5% and 74.3% that of D* for Cyanamid's low and medium density prills respectively.

d) Esso High Density Prills (Terico 34/o/o)

Selected 16mm frames showing the resulting detonation process are shown in Figure 47.

From the constant velocity trace, detonation failure was indicated. Furthermore, the detonation front only propagated through about 3/4 of the hemisphere before dying out.

A massive scattering of unreacted prills is clearly evident in Figure 47d.

e) Western Co-op High Density Prills

These prills failed to propagate a stable detonation front through the hemisphere and a curved trace resulted.

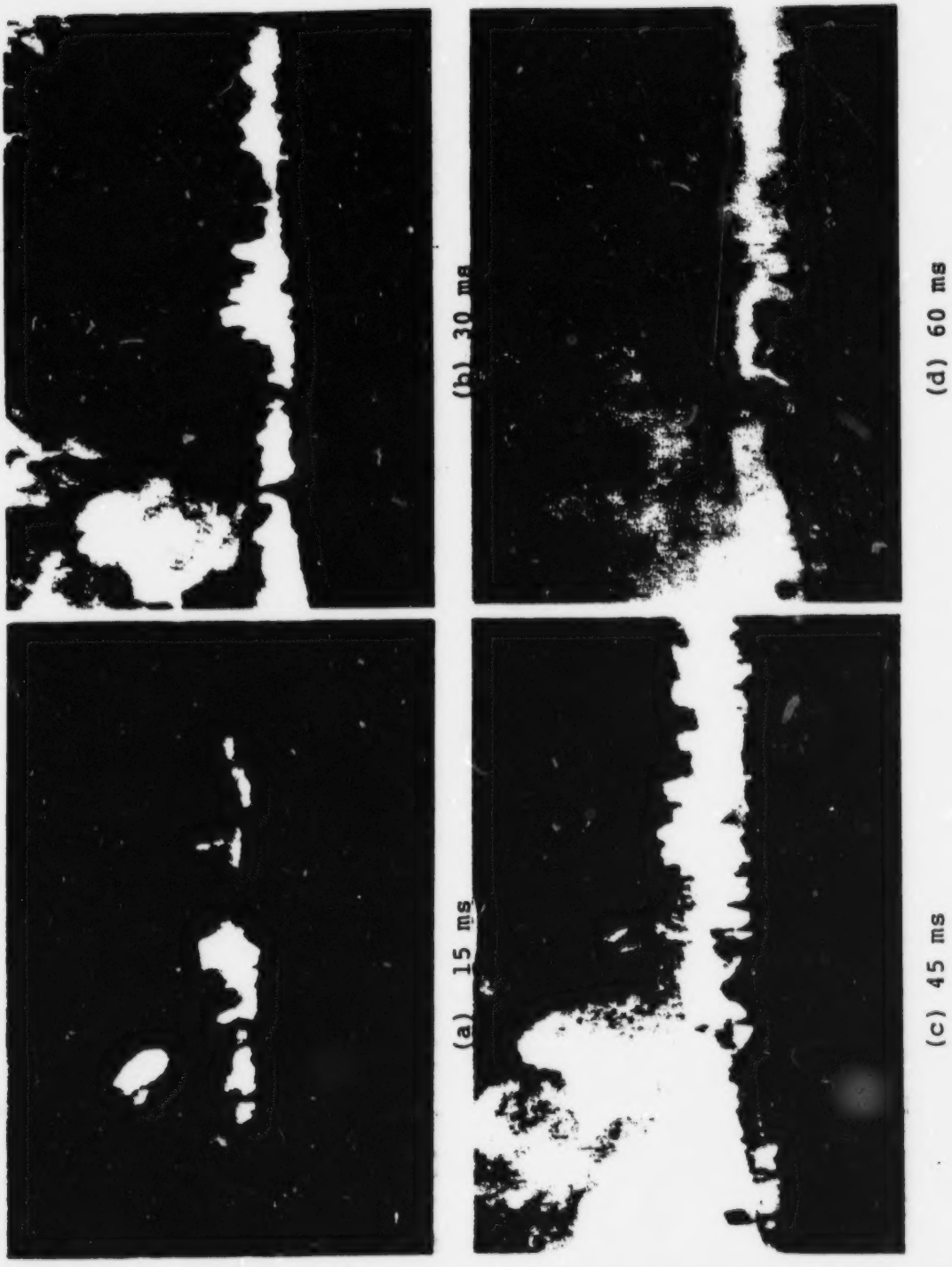


FIGURE 41 ENLARGED 16 mm FRAMES SHOW SMALL AMOUNTS OF UNREACTED PRILLS BEING EJECTED FROM THE DETONATING PILE OF CYANAMID'S C-3 LOW DENSITY PRILLS.

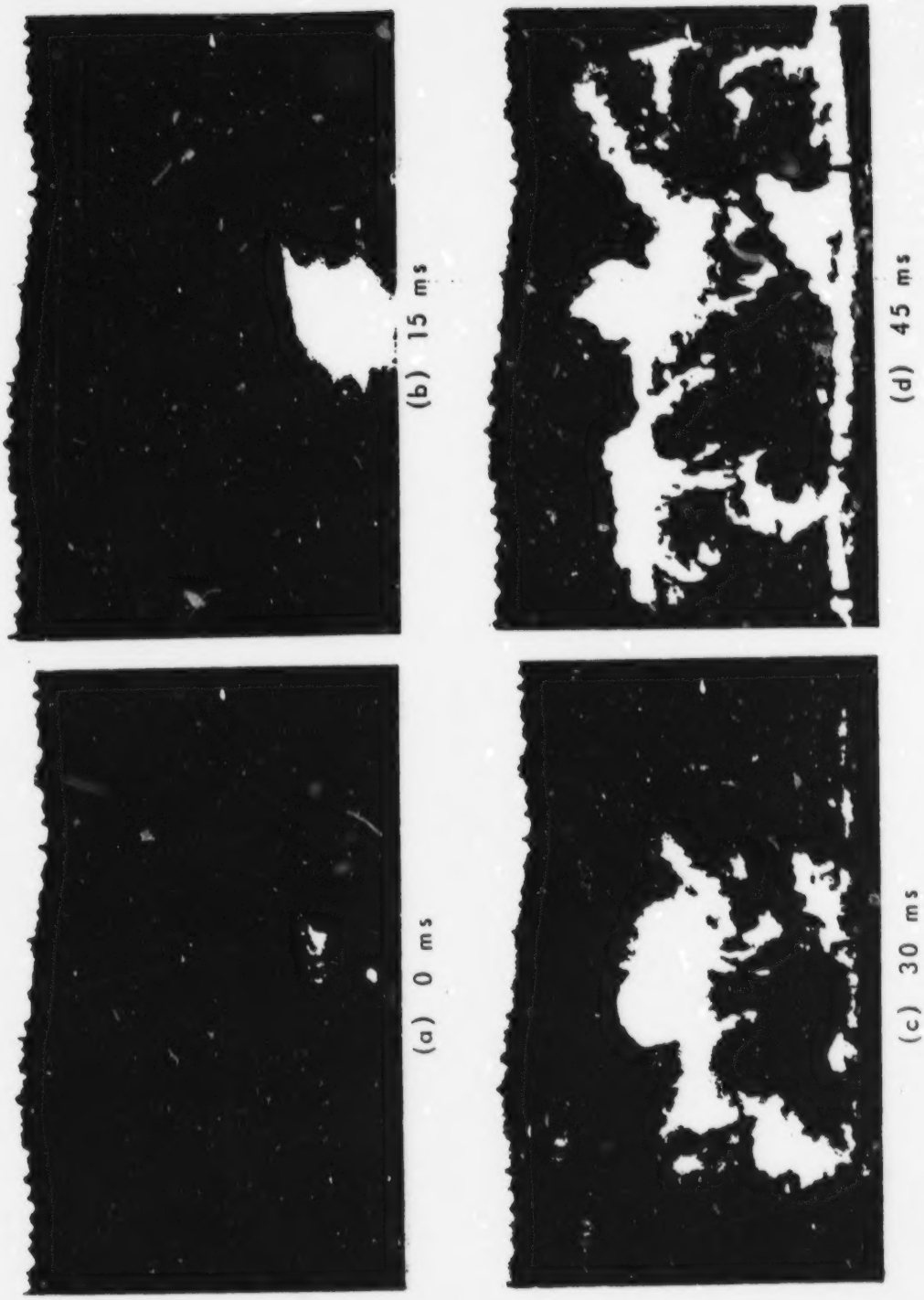
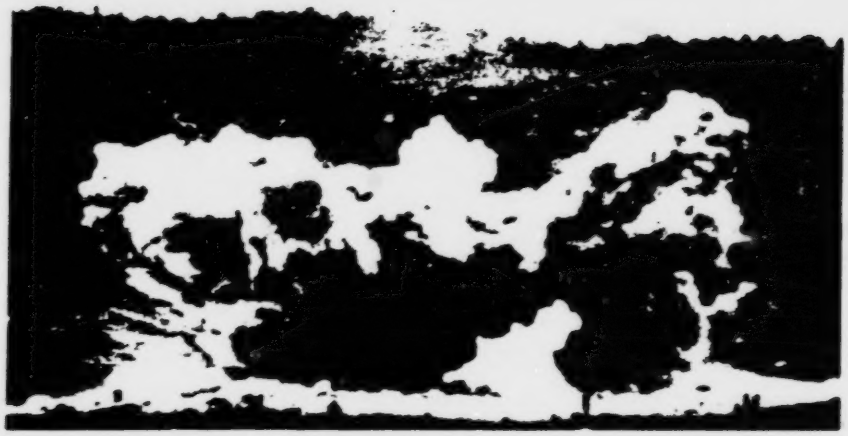


FIGURE 42 ENLARGED 16 mm FRAMES SHOW SOME UNREACTED PRILLS BEING EJECTED FROM THE DETONATING PILE OF CYANAMID'S MEDIUM DENSITY PRILLS (continued)



(e) 60 ms

(f) 75 ms

FIGURE 42 ENLARGED 16 mm FRAMES SHOW SOME UNREACTED PRILLS BEING EJECTED FROM THE DETONATING PILE OF CYANAMID'S MEDIUM DENSITY PRILLS.

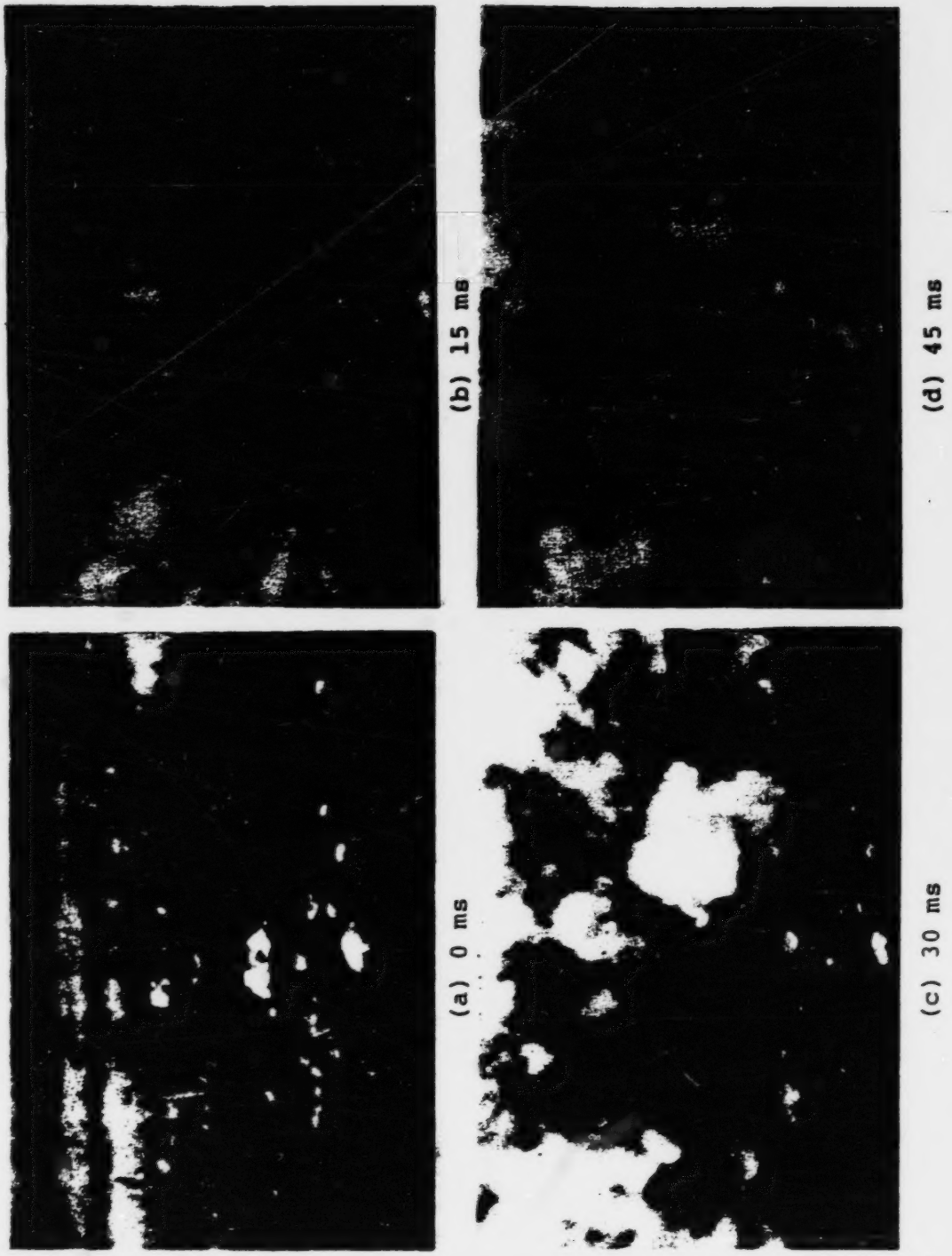


FIGURE 43 ENLARGED 16 mm FRAMES SHOW SIGNIFICANT QUANTITIES OF UNREACTED PRILLS BEING EJECTED FROM THE PILE OF CYANAMID'S REGULAR HIGH DENSITY PRILLS.

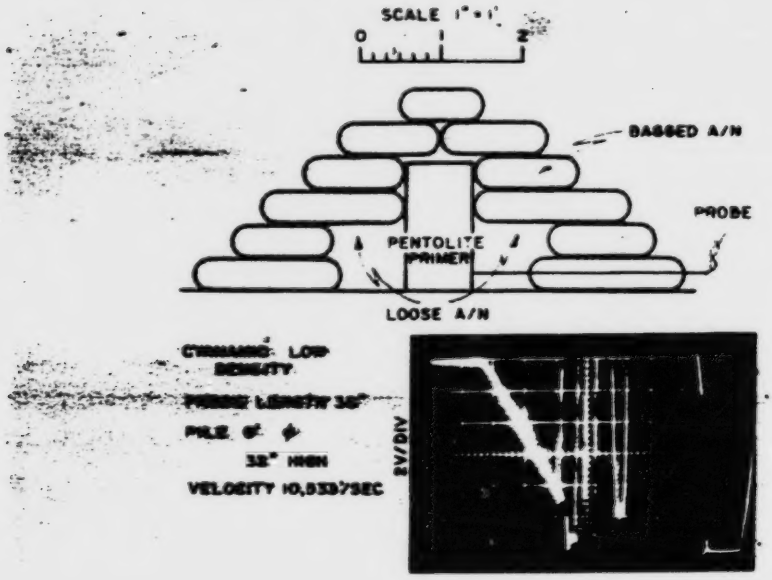


FIGURE 44 RELATIONSHIP BETWEEN OSCILLOSCOPE TRACE OF COLLAPSING PROBE AND PILE GEOMETRY IS SHOWN FOR CYANAMID'S C-3 LOW DENSITY PRILLS.

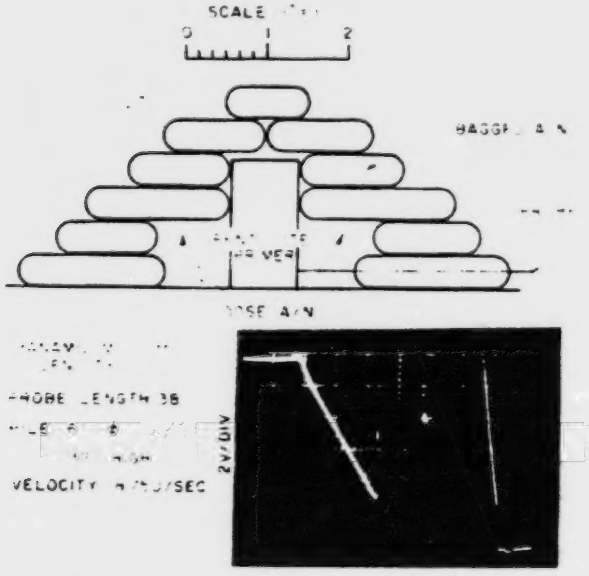


FIGURE 45 RELATIONSHIP BETWEEN OSCILLOSCOPE TRACE OF COLLAPSING PROBE AND PILE GEOMETRY IS SHOWN FOR CYANAMID'S MEDIUM DENSITY PRILLS.

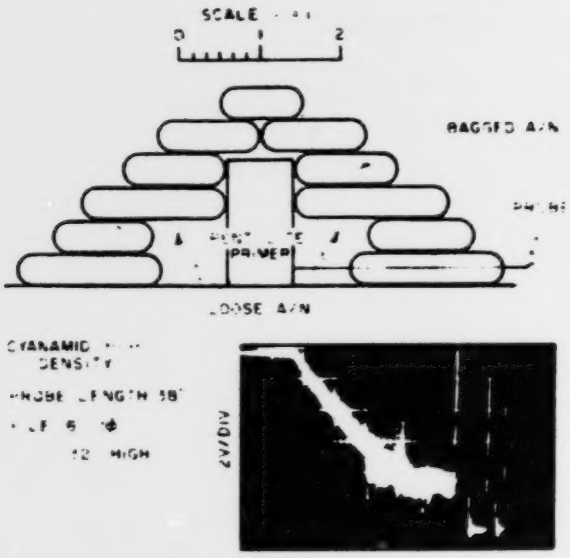


FIGURE 46 RELATIONSHIP BETWEEN OSCILLOSCOPE TRACE OF COLLAPSING PROBE AND PILE GEOMETRY IS SHOWN FOR CYANAMID'S HIGH DENSITY PRILLS.

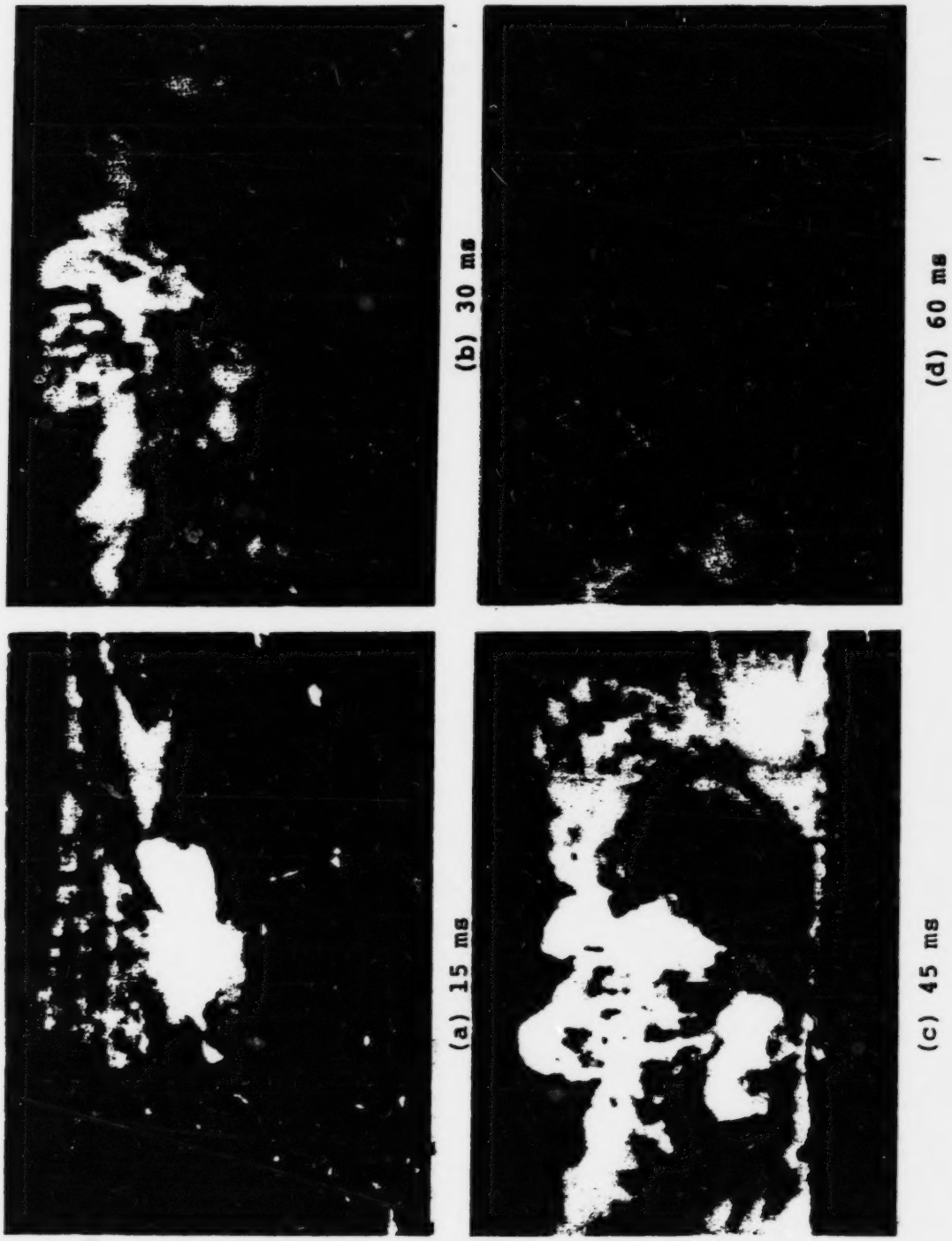


FIGURE 47 ENLARGED 16 mm FRAMES SHOW SIGNIFICANT QUANTITIES OF UNREACTED PRILLS BEING EJECTED FROM A PILE OF ESSO'S HIGH DENSITY PRILLS.

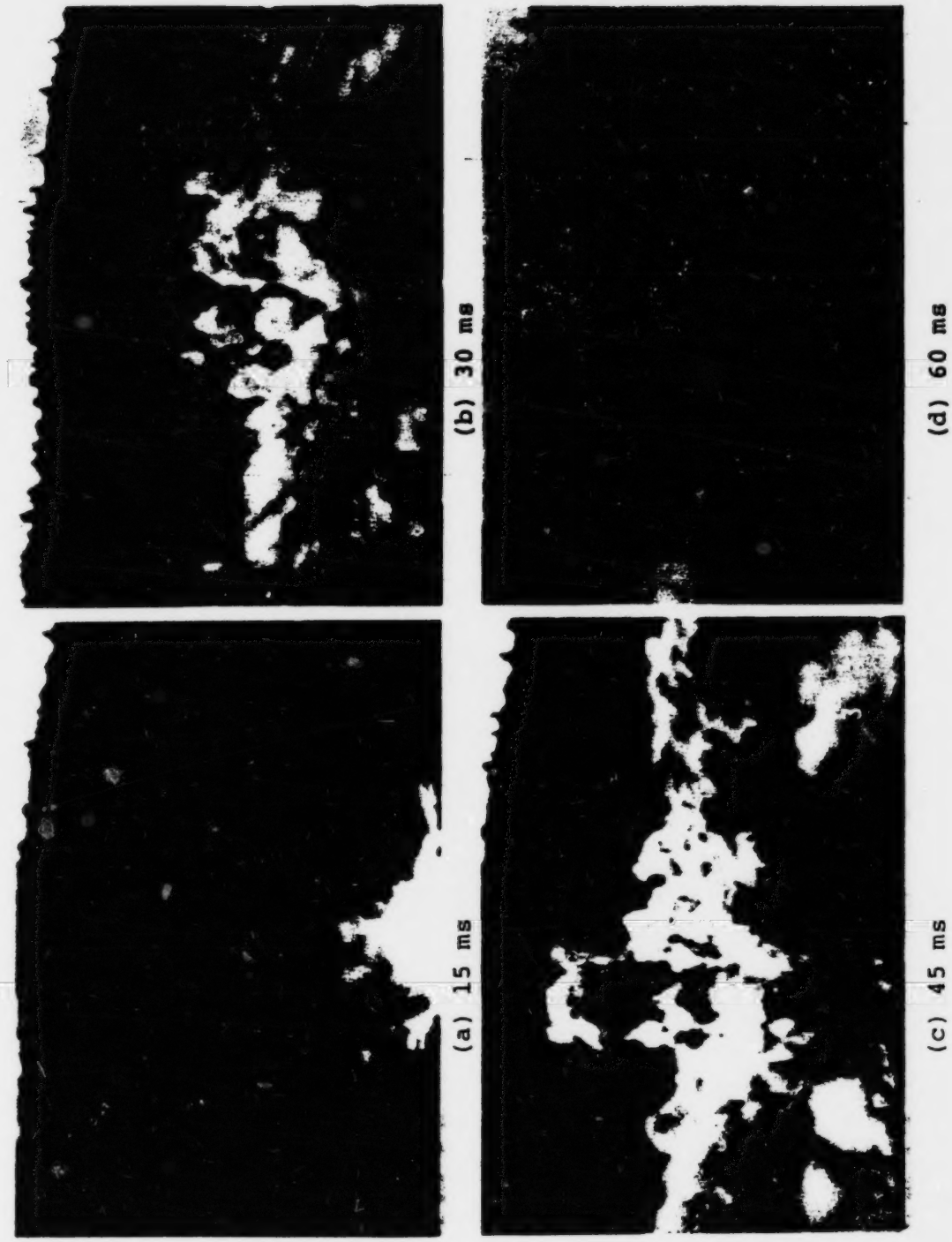


FIGURE 48 ENLARGED 16 mm FRAMES SHOW SIGNIFICANT QUANTITIES OF UNREACTED PRILLS BEING EJECTED FROM A PILE OF WESTERN COOP'S HIGH DENSITY PRILLS.

The detonation front did, however, propagate throughout the entire mass and significantly fewer prills were scattered in this trial than in the Esso Trial, as shown in Figure 48.

The resulting data for these trials is summarized below in Table 9.

TABLE 9

2000 LB HEMISPHERE TEST DATA

PRILL TYPE	BULK DENSITY(ρo) GRAMS/CM^3	D* (M/S)	D (M/S)	N %
CIL LD	.0.80	3400	3290	94
Genstar XP	0.74	3250	3200	97
Cyanamid LD	0.80	3400	3210	89
Cyanamid MD	0.86	3600	2670	55
Cyanamid HD	0.89	3740	F	-
Esso HD	0.91	3760	F	-
Western Co-op HD	0.90	3750	F	-

N is the fraction of the prills reacted inside the detonation head, and therefore able to supply energy for propagation of the detonation front..

16000 Lb Test Series

Western Coop's high density prills were tested in roughly hemispherical configuration (radius of 6 feet) and centrally primed at the bottom with varying amounts of cast TNT. The progress of the detonation process was monitored with continuous velocity probes from the top of the pile.

The actual data relating the bulk density, particle density, coating type and screen analysis for the prills used in each particular trial is given in Table 10.

Table 10

Prill Properties for Each Trial

Trial Number	Date of Delivery	% Coating AC-5	% H_2O	Prill Size Tyler Sieve Retained on Mesh #		ρ_o Grams/cm^3
1	Aug. 3/78	1.27	0.11	6	0.3%	.92
				8	23.4%	
				10	95.3%	
				-12	0.4%	
				-14	0.2%	
				-20	0.1%	
2	Aug. 4/78	1.08	0.08	6	0.6%	.92
				8	32.4%	
				10	94.3%	
				-12	1.7%	
				-14	1.0%	
				-20	0.3%	
3	Aug. 9/78	1.07	0.11	6	0.1%	.92
				8	20.6%	
				10	96.3%	
				-12	0.2%	
				-14	0.0%	
				-20	0.0%	
4	Aug. 10/78	1.05	0.10	6	0.1%	.92
				8	21.3%	
				10	92.5%	
				-12	2.0%	
				-14	1.4%	
				-20	0.5%	

The resultant velocities of detonation recorded for each trial are summarized below in Table 11, and the traces for each trial are shown in Figures 49 to 52.

TABLE 11

Velocity of Detonation of High Density

Ammonium Nitrate Prills

Trial No.	Primer Wt, Lbs.	Bulk Density	D m/s	D* m/s	N %	Time to Consume Pile	Minimum Head Dimension
1	96	0.92gm/cm^3	3460	3800	83	550 µs	1 meter
2	66	"	2420	"	40	900 µs	-
3	32	"	F	"	-	900 µs	-
4	47	"	2140	"	32	900 µs	-

In Trials #2 and #3 there were some unreacted prills around the perimeter of the crater.

In Trial #4 there were scattered prills in the vicinity, but not to the extent of that in Trial #3.

The crater from Trial #1 was the largest with the crater dimensions decreasing with the decreasing yield from each respective trial.

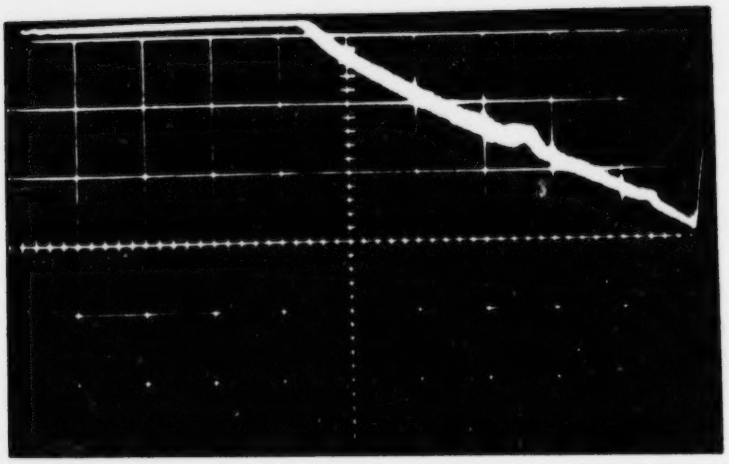


FIGURE 49 OSCILLOSCOPE TRACE OF CONTINUOUS VELOCITY PROBE FOR TRIAL #1 SHOWING A STABLE DETONATION VELOCITY OF 3460 m/s.

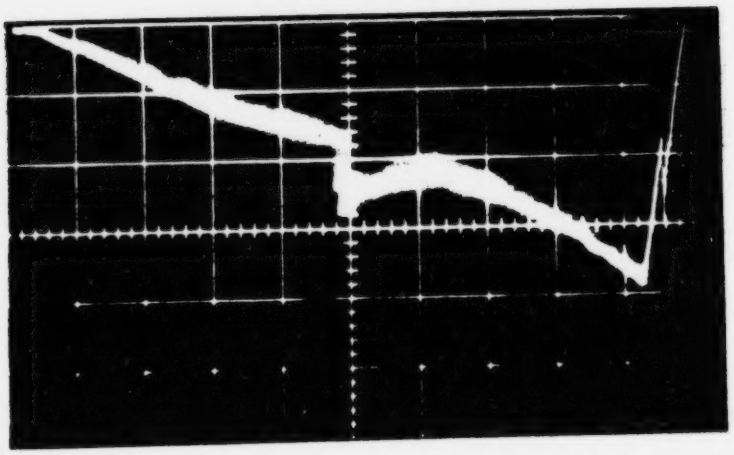


FIGURE 50 OSCILLOSCOPE TRACE OF CONTINUOUS VELOCITY PROBE FOR TRIAL #2 SHOWING AN INCREASE IN DETONATION VELOCITY TOWARDS THE TERMINAL PORTION OF THE PROBE.

NOTE: FOR TRIALS #1 AND #2 THE FOLLOWING DATA APPLIES TO THE ABOVE OSCILLOSCOPE TRACES:

VOLTAGE DROP = 5V/CM
TIME BASE = 100 μs/CM
PROBE LENGTH = 6 FEET

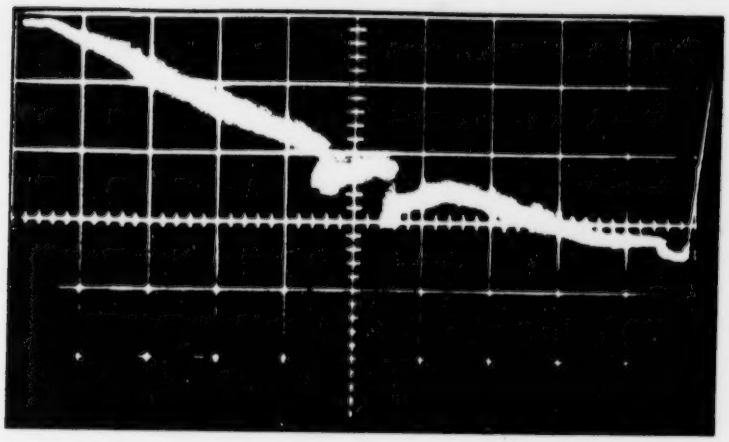


FIGURE 51 OSCILLOSCOPE TRACE OF CONTINUOUS VELOCITY PROBE FOR TRAIL #3 ILLUSTRATING DETONATION FAILURE WHEN PRIMED WITH 32 lbs OF TNT.

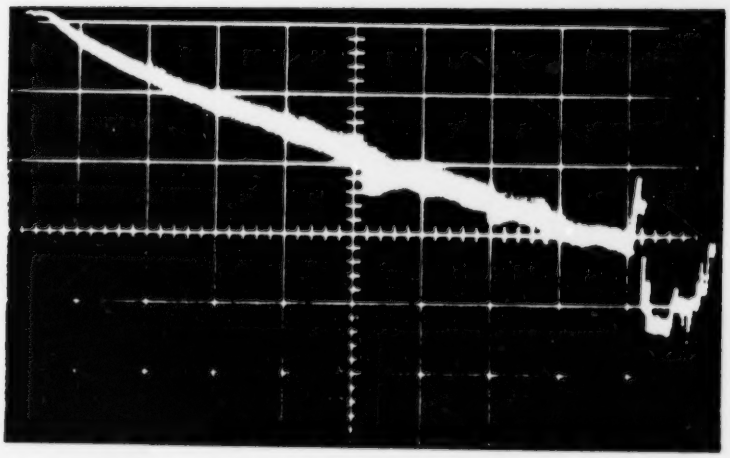


FIGURE 52 OSCILLOSCOPE TRACE OF CONTINUOUS VELOCITY PROBE FOR TRIAL #4 ILLUSTRATING THE DETONATION PROCESS TO BE NEAR FAILURE WHEN PRIMED WITH 67 lbs OF TNT.

NOTE: FOR TRIALS #3 AND #4 THE FOLLOWING DATA APPLIES TO THE ABOVE OSCILLOSCOPE TRACES:

VOLTAGE DROP = 5V/CM
TIME BASE = 100 μs/CM
PROBE LENGTH = 6 FEET.

DISCUSSION

The most significant factor affecting the detonability of ammonium nitrate prills, is density. Density changes as low as 0.10 grams/cm^3 drastically affect both the critical diameter and minimum primer weights. Furthermore, the very large increase in both critical diameter and critical booster weight for prilled ammonium nitrate as the density is raised from 0.80 grams/cm^3 to 0.90 grams/cm^3 is quite significant from a safety standpoint. A 1 lb. TNT primer will most surely initiate a mass of low density ammonium nitrate prills (ρ_o < 0.85 grams/cm^3) provided critical diameter requirements have been met, but will most likely cause a mass of high density prills to fail to detonate completely, when critical diameter requirements have been met.

In the past high density ammonium nitrate prills (ρ_o 0.85 < grams/cm^3) have been regarded as virtually nondetonable unless hammermilled to a lower bulk density and finer particle size, or unless contaminated with reducing agents such as sulphur, aluminum or fuel oil. Nevertheless, once a large enough mass of high density prills has been assembled, and a large enough booster can act over a fairly wide area, i.e. ≈1 meter, even these prills can be made to detonate at a velocity approaching the maximum theoretical obtainable at that particular density.

Critical booster weights of ≈50 lbs. to 100 lbs. of TNT are large compared to the 1 lb. or so required to initiate low density prills, but

a pool of molten ammonium nitrate of 200 lbs. to 300 lbs. can easily accumulate under fire exposure. The complete detonation of 200 lbs. - 500 lbs. of molten ammonium nitrate (at a density of 1.0 grams/cm^3 to 1.4 grams/cm^3) in contact with a burning bulk storage pile of high density prills (ρ_o > .85 grams/cm^3) can initiate a detonation in most if not all of the pile.

The gradual increase in detonability exhibited in these tests by dense prills clearly shows the influence of charge diameter on detonation stability. In the one ton series for example, the fact that even under the influence of very heavy boostering, high density prills failed to detonate, clearly shows propagation failure to be the result of a diameter effect.

Once critical diameter requirements have been met for the high density prills, the ability of the high density prills to be initiated becomes very dependent upon receiving a large enough stimulus. This is predominantly the result of the very sluggish nature of the reaction with non-porous prills where available reaction sites on the prill surface are very few. Detonation stability can then exist only if enough of these prills are reacted over a sufficiently large area, and detonation failure can occur even though as much as 40 lbs. of TNT or its energy equivalent is used.

CONCLUSION

According to Cook (24), a rarefaction wave travels behind a detonation front at ≈ 5/8 D. Since ammonium nitrate prills characterized by bulk densities of ≈ 0.90 grams/cm^3 experience detonation failure in a hemispherical pile of radius ≈ 1 meter but detonate completely (when adequately primed) in hemispherical piles of radius ≈ 2 meters, the critical diameter for prills of this type is estimated to be between approximately 1 meter and 2 meters.

The critical booster weight for high density ammonium nitrate prills is at least 50 lbs. to 70 lbs. of TNT or its energy equivalent when assembled in hemispherical geometry.

For low density or explosive grade ammonium nitrate prills, where ρ_o ≈.8 gms/cm^3 critical booster weights of ≈ 1 lb. of TNT are necessary to initiate a detonationg in a charge 4 inches - 5 inches in diameter, under strong confinement (23)

On the basis of tests conducted on high density prills of low porosity, it is necessary to react a very high percentage of prills inside the detonation head in order that a stable detonation be obtained, and this is largely dependent upon receiving very heavy stimulus very early in the detonation process.

Ammonium nitrate prills, once assembled in a mass of sufficiently large diameter and given adequate priming, will detonate completely regardless of porosity, and without any organic contamination whatsoever.

6. PROJECTILE IMPACT INITIATION OF AMMONIUM NITRATE AND AMMONIUM NITRATE-BASED FERTILIZER SOLUTIONS

Ammonium nitrate has been involved in a series of major accidents, most frequently during fire exposure. It is reasonable to assume therefore, that the shock sensitivity of the molten material (m.p.170°C) could be a factor in the initiation of ammonium nitrate under these conditions, and its sensitivity to impact from low amplitude shocks needs to be investigated.

Shock sensitivity to low amplitude shocks is best determined by projectile impact tests, especially large diameter projectiles travelling at less than 500 m/s.

However, the results of projectile impact tests can be strongly influenced by the geometry of the tests, hence careful control of the experiments must be made if the results are to be interpreted generally.

If the sensitivity to low amplitude shocks of molten ammonium nitrate, ammonium nitrate-based fertilizer solutions, and other sensitizing liquours such as E.G.M.N. and M.A.N. can be determined, various parameters affecting the construction of transfer lines, storage and transport containers, as well as, in the case of ammonium nitrate, the geometry of storage sheds and buildings can be more explicitly designed.

EXPERIMENTAL

1) PROJECTILE AND CANNON GEOMETRY

Projectile impact parameters were determined by firing cylindrical aluminum projectiles at ammonium nitrate melts and ammonium nitrate-based fertilizer solutions contained in pyrex glass containers, with a wall thickness of 3mm.

The cannon and projectile dimensions are shown below in Tables 12 to 14 . Only the 150mm projectile was used in the testing of the ammonium nitrate-based fertilizer solutions.

The vessel diameter was 180mm for the 150mm and 25mm tests and 125mm for the 50mm tests. All had a length of 600mm. The vessels were wrapped with nichrome heating coils and covered with fibreglass insulation.

A stainless steel thermocouple was inserted into the vessel through a filling hole in the top of the receptor vessel to monitor the temperature, as shown in Figure 53 below.

The aqueous solutions were not preheated, and their densities were lowered to 0.80 gms/cm^3 with the addition of glass bubbles, the properties of which are shown below in Table 15.

The projectile velocity was monitored with either copper timing wires or aluminum foil contacts.

TABLE 12

150mm CANNON DIMENSIONS

BARREL:	LENGTH	3m
	1.D	152mm
	0.D	178mm
CHAMBER:	LENGTH	1m
	1.D	125mm
	0.D	178mm
PROJECTILE:	LENGTH	150mm
	DIAM.	150mm
	MASS	7,200gm.

PROPELLANT: PRIMACORD INITIATED BY CXA No. 8 ELECTRIC BLASTING CAP

TABLE 13

50 mm CANNON DIMENSIONS

BARREL:	LENGTH	1.2m
	I.D.	51 mm
	O.D.	76 mm
PROJECTILE:	LENGTH	100 mm
	DIAM.	50 mm
	MASS	500 gm

PROPELLANT: DETRAPRIMES INITIATED BY CXA No. 8 ELECTRIC BLASTING CAP

TABLE 14

25mm CANNON DIMENSIONS

BARREL:	LENGTH	1.2m
	I.D	25.4mm
	O.D.	51 mm
PROJECTILE:	LENGTH	50 mm
	DIAM.	25 mm
	MASS	70 gm.

PROPELLANT: 4F BLACK POWDER BY GOEX, INITIATED BY CXA S140 SQUIB

THIS CANNON WAS SET UP THE SAME AS THE 50mm CANNON EXCEPT A HIGH PRESSURE STEEL PLUG WAS USED IN THE END OF THE CANNON BARREL INSTEAD OF A CAP. TO LOAD THE CANNON, THE SQUIB WAS PLACED IN THE END OF THE BARREL AND THE LEAD WIRE PASSED THROUGH A SMALL HOLE IN THE STEEL PLUG. AFTER THE PLUG WAS SECURELY SCREWED IN, BLACK POWDER WAS POURED IN THROUGH THE OPPOSITE END OF THE BARREL. FIBERGLASS INSULATION USED FOR WADDING AND THE PROJECTILE WERE THEN TAMPED DOWN THE BARREL.

TABLE 15

PROPERTIES OF GLASS BUBBLES (3M)

NORMAL BULK DENSITY = 0.10 gm/cc

SIZE = 90% BY VOLUME BETWEEN 20 AND 130 MICRONS

NOMINAL DIAMETER - 90 MICRONS

WALL THICKNESS - 0.5 MICRONS

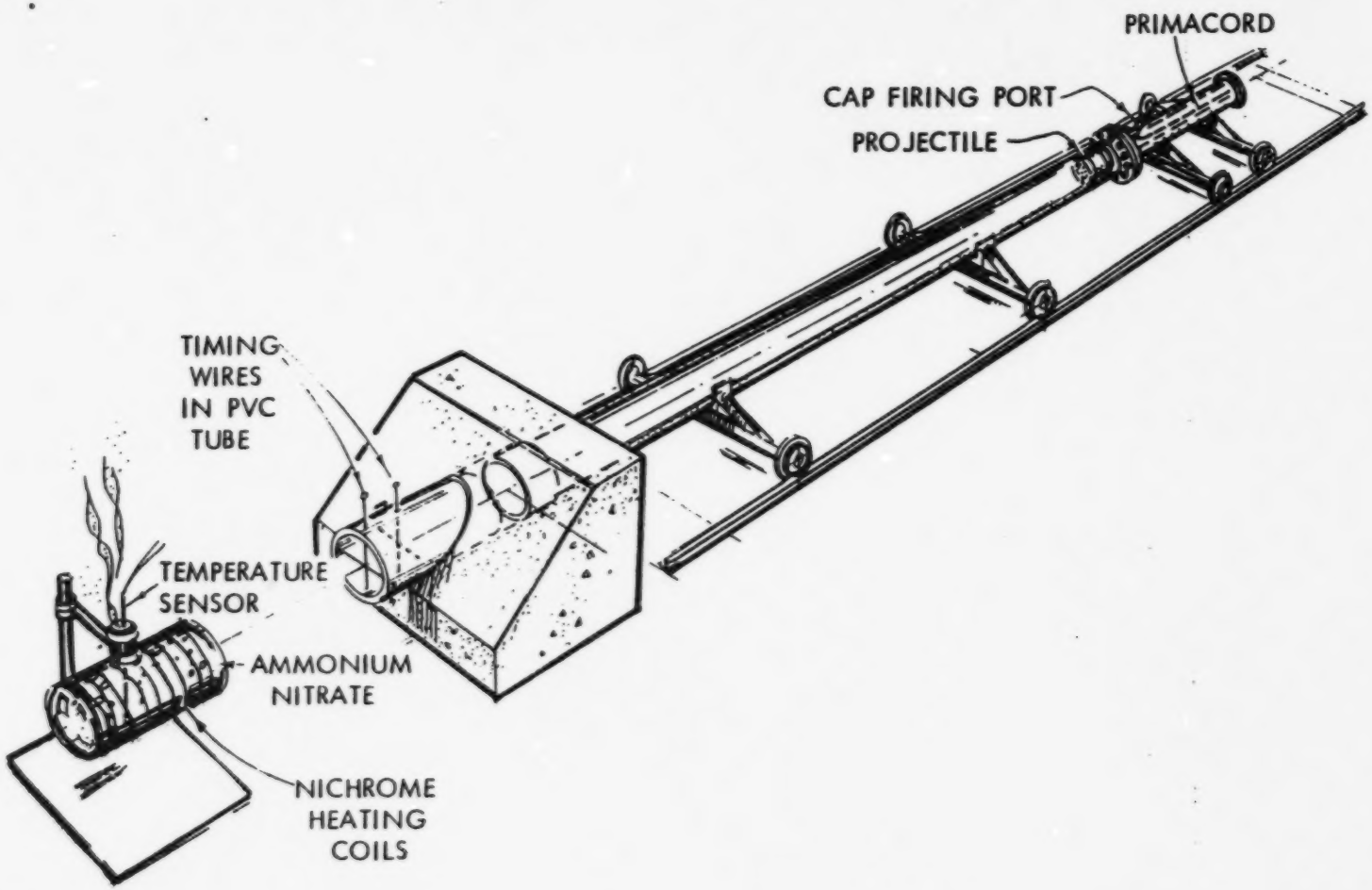


FIGURE 53 : (a) 150 mm CANNON TEST LAYOUT.

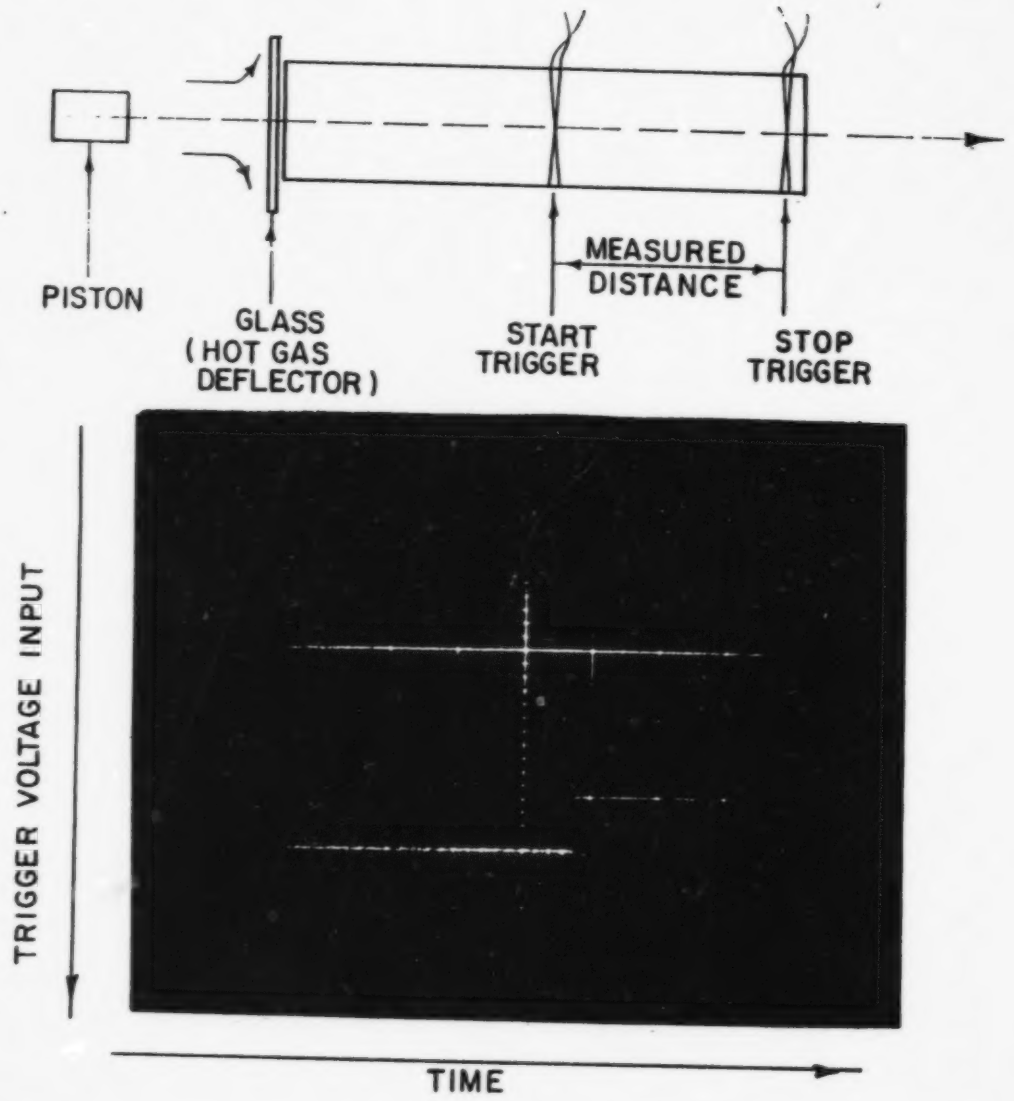


FIGURE 54: TYPICAL OSCILLOSCOPE TRACE USED FOR PROJECTILE VELOCITY CALCULATIONS.

A system was set up such that the projectile would hit the first set of wires (or foil) thereby closing an electric circuit, which in turn started an oscilloscope trace.

Projectile contact with the second wire would introduce another pulse to the oscilloscope. From the time between the pulses for a given separation of the wires, the velocity can be calculated. The oscilloscope trace was recorded on a polaroid photograph as shown in Figure 54.

2) AMMONIUM NITRATE AND AMMONIUM NITRATE-BASED FERTILIZER SOLUTIONS

The ammonium nitrate used was uncoated AN prills from CIL.

The composition of the fertilizer solutions tested is shown below in Table 16.

TABLE 16

AMMONIUM-NITRATE-BASED FERTILIZER SOLUTIONS

MATERIAL	COMPOSITION (Weight %)	DENSITY (GMS/cm^3)	
		with glass bubbles	without glass bubbles
AN/Urea/H_2O	47/38/15	1.0	1.36
AN/NH_3/H_2O	65/22/13	1.0	1.15
E.G.M.N./H_2O	81/19	1.0	1.32
M.A.N./H_2O	79/21	.8-1.0	1.24

DATA FROM PROJECTILE IMPACT TESTS

TABLE 17

PROJECTILE IMPACT TEST

CANNON 150mm

AN/Urea/H_2O (47/38/15)

Density: - as received 1.36gms/cm^3
FAILED Piston speed 1,422 fps

Density: - G.B. 1.0gms/cm^3
FAILED Piston Speed 1,213 fps

AN/AMMONIA/H_2O (65/22/13)

Density: - as received 1.15gms/cm^3
FAILED Piston Speed 1,398 fps

Density: - G.B. 1.0gms/cm^2
FAILED Piston Speed 1,200 fps

E.G.M.N./H_2O (81/19)

Density: - as received 1.32gms/cm^3
FAILED Piston Speed 1,374 fps

Density: - G.B. 1.00gms/cm^3
FAILED Piston Speed 1,092 fps

MAN/H_2O (79/21)

Density: - G.B. 1.00gms/cm^3
FAILED Piston Speed 1,278 fps

Density: - G.B. .8gms/cm^3
FAILED Piston Speed 1,082 fps

CONCLUSIONS

Regarding the ammonium nitrate based fertilizer solutions, none were capable of being initiated in the projectile impact tests, due mainly to the large unconfined critical diameters of these solutions. This alone would tend to indicate that the hazard presented by such solutions when impacted by rapidly moving projectiles is very small, since piston speeds as high as 433 m/sec with the 150mm projectile were incapable of initiating these unconfined solutions.

The E.G.M.N. liquors, without glass bubbles did not initiate at the projectile velocity of 419 m/s, nor did the solutions with glass bubbles (ρ_o = 1.0 gms/cm^3) when impacted with a projectile travelling at 332 m/s. However, not enough tests were conducted to be able to establish statistically the true V_{50} curve where V_{50} is the critical impact velocity required for a 50% probability of initiation.

The hazard presented by the shock initiation of the ammonium nitrate-based fertilizer solutions or the M.A.N. - E.G.M.N. liquors is more likely to occur in the confined state given the manner in which these solutions are stored and transported, hence all future projectile work should be done on the confined receptors. From the data accumulated with unconfined receptors, the probability of initiation by projectile impact of unconfined or lightly confined solutions is also highly remote, especially in view of the large, unconfined critical diameters (25).

TABLE 18

MINIMUM PRIMER DATA OBTAINED FROM TESTS ON AMMONIUM NITRATE SOLUTIONS

SOLUTION CONCENTRATION WEIGHT % AMMONIUM NITRATE	WEIGHT % WATER	TEMP °C	DENSITY gm/cc	PRIMER WEIGHT gms	RESULT
95	5	120	1.0	0.8	FAILED
95	5	120	1.0	4.8	FAILED
93	7	160	0.81	0.8	DETONATED
93	7	120	1.0	0.8	FAILED
90	10	100	0.8	0.8	DETONATED
90	10	130	0.83	0.8	DETONATED
90	10	128	1.0	0.8	FAILED
90	10	118	1.0	4.8	FAILED
90	10	125	1.0	24.8	FAILED
80	20	120	0.8	0.8	FAILED
80	20	140	0.8	0.8	FAILED
80	20	135	0.8	8.8	FAILED
80	20	140	0.8	24.8	FAILED
80	20	127	0.8	70.8	FAILED

TABLE 19

150 mm CANNON TEST RESULTS

SAMPLE WEIGHT % AMMONIUM NITRATE	TEMP °C	DENSITY gm/cc	PROJECTILE IMPACT VELOCITY (m/s)	RESULT
100	260	0.8	66	FAILED
100	260	0.8	122	FAILED
100	260	0.8	190	DETONATED
100	240	1.32	255	FAILED
100	240	1.32	335	FAILED
100	240	1.32	365	FAILED
100	240	1.32	365	FAILED
95	130	0.8	190	FAILED
95	130	0.8	305	FAILED
95	130	0.8	365	FAILED
95	130	0.8	365	FAILED

However, from the data shown in Tables 18 and 19 (26), it can be seen that molten ammonium nitrate is impact sensitive in that detonations were obtained at 260°C when impacted at velocities of 190 meters/second with the 155mm (and 50mm) projectiles. Furthermore, this corresponds to an induced shock impact pressure of about 1 Kilobar acting for a duration of about 1 microsecond. It should also be pointed out that in the geometry tested, the molten AN is essentially unconfined. This data would thus tend to indicate that molten ammonium nitrate at elevated temperatures is an extremely shock sensitive and hazardous material, and in the confined state, would be even more so. This has been amply demonstrated by the small, high velocity projectile impact work conducted by the U.S.B.M. on molten ammonium nitrate (4).

The presence of small percentages of water however, have a great desensitizing effect, and no detonations were obtained on 95/5 AN/water mixes at densities of $\cong 0.8$ gms/cm^3 at maximum cannon velocities approaching 400 meters/second. The same mixture is, however, cap sensitive.

7. INITIATION-TO-DETONATION OF MOLTEN AMMONIUM NITRATE BY DEFLAGRATING TYPE COMPOSITIONS

INTRODUCTION

The ability of ammonium nitrate to undergo a transition to detonation from a purely burning mode is one of the most perplexing and least understood characteristics of this material. The deflagration to detonation transition (abbreviated as DDT) has been studied in detail for cast, shock-sensitive explosives by Donna Price and Richard Bernecker at the Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland for many years (27). In their studies with shell fillers, DDT starts as a mild thermal ignition of the explosives charge at one end of a closed tube. It was observed that containment of any combustion gases is a necessary but not sufficient requirement for a transition to detonation to occur for secondary explosives.

In their studies a model was successfully developed which was based on a mechanism consisting of two distinct processes. First, there must be a sufficiently rapid pressure increase in the ignition region to produce an incipient shock wave at some point beyond the ignition region. Secondly, the unburned explosive beyond the burning region must be sufficiently shock sensitive to be initiated by a shock wave equal in amplitude to the high pressure achieved in the burning region.

In the case of porous explosives, preliminary experiments by Griffiths and Groocock (28) revealed that there is an additional heat transfer mode which may affect the transfer of energy from the ignition area into the unburned explosive. This mode was called convective burning and it depends in part on the permeability of the explosive charge. Thus, pores which are interconnected form a path allowing the penetration of hot combustion gases from the ignition region deep into the unburned explosive charge. Griffiths and Groocock observed optically the propagation of a convective flame front at a rate of about 1mm/μ Sec for some distance within the charge before the formation of a detonation front.

Molten ammonium nitrate may in fact resemble a very porous explosive charge not unlike the ones described above.

Therefore, some important objectives of this study were to:

i) attempt to deduce information concerning the DDT mechanism(s) in porous (aerated) molten ammonium nitrate (at elevated temperatures) from the experimental results;

ii) observe whether transitions from burning to detonation can occur in molten ammonium nitrate at lower temperatures (i.e. 170°C < T < 260°C);

iii) observe whether transitions from burning to detonation can occur in molten ammonium nitrate at any temperature in the unconfined state.

EXPERIMENTAL DETAILS

1. DEFLAGRATING COMPOSITIONS BASED ON AMMONIUM NITRATE

Under conditions of fire exposure contaminants likely to form deflagrating mixtures with ammonium nitrate include: charcoal (from paper, wood, etc.); organic fuels such as diesel oil, plastics, polyethylene (from bags, etc.); aluminum (from conduit or wiring); and copper (from wiring, etc..).

The reaction of ammonium nitrate with these types of materials would be expected to be more violent and rapid if the ammonium nitrate is in the molten state than at ordinary temperatures. Yet it is in the molten state that reaction is most likely to occur under conditions of fire exposure.

In this laboratory, rapid heating tests were conducted on mixtures of ammonium nitrate with contaminants similar to the types described above.

In a series of tests, 50 gram samples of ammonium nitrate with organic and metallic contaminants were rapidly heated in 500 ml round bottom Pyrex flasks using a large gas burner. The results are given below in Table 20.

TABLE 20

RAPID HEATING TEST RESULTS FOR AMONIUM NITRATE MIXTURES CONTAINING ORGANIC AND METALLIC CONTAMINANTS 50 GRAM SAMPLES

TEST NUMBER	COMPOSITION		OBSERVATIONS
1	AN	100%	Melting and accumulation of vapors above AN which turned red brown then exploded. AN ignited at edges and entire surface burned until AN consumed. No explosion.
2	AN	80%	
	Pb Powder	20%	Melting and accelerated decomposition relative to Test #1; considerable foaming; no explosion.
3	AN	80%	
	Cr Powder	20%	Accelerated decomposition even faster than Test #1 or #2; considerable foaming; no explosion.
4	AN	90%	
	Cu	10%	Accelerated decomposition relative to Test #1; Blue-green mass formed; Rapid propellant-like burning of residual towards end after AN reacted; Evaluation of considerable black smoke (CuO)
5	AN	80%	
	Zn	20%	Violent deflagration after on set of melting. Considerable reaction. No explosion.
6	ANFO	80.0%	
	Zn	20.0%	Violent deflagration after on set of melting. Considerable reaction and propellant like burning of residual mass.

TEST NUMBER	COMPOSITION	OBSERVATIONS
7	ANFO 100%	Slight audible puffs and orange flashes after melting and ignition of vapors.
8	ANFO 77%	Rapid on set of deflagration of AN and Cu followed by ignition of residual mass. No explosion.

These tests indicate that metals such as Cu and Zn, especially the later, react violently and even explosively with molten ammonium nitrate. Furthermore, the exothermic reaction between ammonium nitrate and fuels such as diesel fuel is enhanced or accelerated by the presence of metals such as Cu and Zn.

Compositions such as the types described above could serve as sources of potential dangerous hot spots in pool fires involving molten ammonium nitrate.

2. INITIATION OF DETONATION IN MOLTEN AMMONIUM NITRATE USING CONFINED AND UNCONFINED DEFLAGRATING COMPOSITIONS

In an attempt to initiate a detonation in molten ammonium nitrate using confined and unconfined deflagrating compositions several exploratory trials were conducted using 4F Black Powder, and a finely powered composition based on ammonium nitrate consisting of: ammonium nitrate, 80%; charcoal, 10%; and aluminum, 10%.

In Trial #1 80 grams of 4F Black Powder was confined in a schedule 40 steel pipe (1"diameter, 4" long), capped at both ends. The Black Powder was ignited by means of a pyrotechnic squib located at the center of the pipe.

In Trial #2 80 grams of the above described composition based on ammonium nitrate was similarly confined. Additional ignition was provided by 2 to 5 grams of a $Mg/Ba(NO_3)_2$ mixture wrapped around the squib by means of aluminum foil.

In Trial #3 250 grams of the above ammonium nitrate-based composition was confined in a 2" schedule 40 pipe, 8" long, and ignited in a manner similar to that of Trial #2.

In all three trials, 25 lbs. of molten ammonium nitrate was contained in an aluminum pot 12" in diameter and 12" deep. The molten ammonium nitrate was brought to the desired temperature of 260°C by means of a propane torch immediately

beneath the pot, the temperature being monitored by a thermocouple. When the molten ammonium nitrate had reached the desired temperature, the pipe containing the priming composition was lowered to the bottom of the pot and fired immediately. The event was observed by means of a LOCAM camera at 500 frames/second.

In the Black Powder Trial, a violent explosion (most probably a detonation) shredded the aluminum pot and produced a small crater in the ground.

In Trial #2, only a dispersion of the molten ammonium nitrate resulted. The pipe was recovered with no damage other than a piece of the end cap being blown off.

In Trial #3, a violent explosion (also most probably a detonation) shredded the container and produced a slight crater in the ground.

These trials served to indicate that it is possible to initiate an explosion (and most likely a detonation) in molten ammonium nitrate by means of deflagrating type composition, providing the molten ammonium nitrate is at the correct temperature, and that sufficiently large quantities of priming compositions are used.

The confinement provided by the steel pipe may have complicated events somewhat, however, and a further series of trials were conducted using only 4F Black Powder contained in thin wall polyethylene bottles.

a) Initiation of Detonation in Molten Ammonium Nitrate Using Black Powder Contained in Polyethylene Bottles.

200 grams of 4F Black Powder contained in thin walled "Nalgene" polyethylene bottles (125 ml capacity) were used in this series of tests in an attempt to bring about a detonation in the molten ammonium nitrate using unconfined (of very lightly confined) charges.

This bottle was wrapped lightly with aluminum foil and a 1/2 lb. lead weight attached to assist in lowering the container to the bottom of the vessel containing the molten ammonium nitrate.

The charge was ignited with a pyrotechnic squib, the lead wires of which were insulated from the high temperatures by means of aluminum foil.

The procedure involved lowering the bottle into the vessel as quickly as possible when the charge had reached the desired temperature. The squib was then initiated immediately and the event captured on High Speed Film using a HYCAM camera at 1000 frames/second.

The steel vessels used to contain the molten ammonium nitrate initially were 5" in diameter with a 1/2" wall and 16

inches long. These were wrapped with 2" thick fiberglass.

Heating was done with a propane torch, located beneath the container.

The results are summarized in Table 21 below.

TABLE 21

INITIATION TESTS ON MOLTEN AMMONIUM NITRATE

USING UNCONFINED BLACK POWDER

TEST NUMBER	MOLTEN AN TEMPERATURE	OBSERVATIONS
1	264°C	No violent explosion although a loud explosion was heard and considerable deformation of the base of the container resulted.
2	270°C	Violent explosion; fragmentation of container; deep crater in ground. Probable detonation.
3	284°C	Loud explosion; container remained intact although severely deformed on end; container violently propelled into ground crushing support bricks.

These trials provided some interesting results, in that even though no violent shredding of the container occured in Trials #1 and #3, a loud explosion was heard which differed considerable in amplitude from that of the Black Powder priming charge alone. Also, the containers were violently propelled into the ground, even more so in Trial #3 than Trial #1.

On the basis of these preliminary trials, it is possible to bring about a detonation in confined molten ammonium nitrate at high temperatures using lightly confined deflagrating mixtures such as Black Powder.

CONCLUSIONS

Tests conducted with molten ammonium nitrate and powdered metals, as shown in Table 20 reveal Cu and Zn to be the most hazardous with respect to promoting violent exothermic reactions, with Zn being the most reactive and violent. When organic materials were present, these exothermic reactions proceed very rapidly, quite unlike the same compositions at ambient temperatures of approximately 20°C.

Confined ignition of deflagrating compositions of AN/C/AL by means of $Mg/Ba(NO_3)_2$ and/or Black Powder ignitors generally resulted in a rapid burning of the composition and caused the end cap(s) of the confining pipe to be blown off.

The pipe itself, however, showed no visible signs of deformation, and the composition did not detonate, but merely deflagrated.

When these pipes were lowered into the molten ammonium nitrate at 260°C and the priming charge ignited, a probable detonation occurred in the molten ammonium nitrate only when ≈ 250 grams of mixture was used. When 80 grams of mixture was used there was a loud report but no violent explosion or detonation. They may indicate that the critical primer weight for a composition of this type lies somewhere between 80 and 250 grams under the conditions tested, but more tests would have to be done to confirm this.

When 80 grams of 4F Black Powder were placed a capped 1" diameter, 4" long schedule 40 pipe, and lowered into molten ammonium nitrate at 260°C as described above and ignited, the ammonium nitrate appeared to undergo a detonation.

Black Powder is capable of fragmenting these pipes rather violently, and the resultant explosion may be quite sufficient to impart a critical particle velocity in the molten ammonium nitrate of ≅500 meters/second.

By removing the confinement and relying mainly upon the heat flux and modest pressures developed by deflagrating 4F Black Powder, it was possible to initiate a strong explosion (most likely a detonation) in molten ammonium nitrate at 270°C. This represents a drop in shock pressure of several orders of magnitude with respect to a #6 Electric Blasting Cap. It also represents a considerable increase in net energy, considering that ≅ 200 grams of 4F Black Powder was used.

Unconfined mixtures of ammonium nitrate with organic compounds such as charcoal, polyethylene, or paper can also serve as sources of potential hot spots in fires involving molten ammonium nitrate. When confined, these mixtures react explosively when ignited.

Exploding pipes containing deflagrating compositions such as ammonium nitrate/C/Al or 4F Black Powder appear to be

capable of initiating a detonation in molten ammonium nitrate at certain temperatures and if present in sufficiently large quantities. The pressures represent a significant drop in that available from blasting caps or high explosive primers such as Detraprimes or Pentolite, although the total energy release is comparable or greater than some blasting caps or high explosive primers tested.

However, the ability of unconfined Black Powder to initiate a probable detonation in molten ammonium nitrate is very significant and more closely approximates the requirements of the proposed DDT theory previously described. Further testing in this area would be needed to evaluate fully a DDT mechanism.

In order to determine what peak pressures might be expected in the explosion of black-powder in a water-glass bubble mix used to simulate molten AN at 260°C, pressure transducers were used to measure the peak pressures recorded at certain distances from the bottom face of the polyethylene bottles.

While the shock duration was not measured, it is clear that near the bottle itself, pressures of 10,000 - 14,000 PSI may be expected, and this can be of sufficient amplitude to cause initiation, provided the duration of the pulse is not too

short, as shown in Table 22 and Figure 55 below.

Thus, under certain conditions of confinement and size, even certain deflagrating compositions may be expected to provide thresholds for initiation of molten ammonium nitrate to detonation depending on the temperature regime of the molten ammonium nitrate and size geometry.

TABLE 22

PRESSURE-DISTANCE RELATIONS
FOR BLACK POWDER IGNITED
IN WATER-GLASS BUBBLE MIX

WATER-GLASS BUBBLE DENSITY	=	0.8 gms/cm^3
* SAMPLE SIZE OF BLACK POWDER	=	200 grams
BLACK POWDER CONTAINER	=	POLYETHYLENE

DISTANCE FROM POLYETHYLENE BOTTLE (BOTTOM FACE) INCHES	MEASURED PRESSURE (PSI)
2	905
4	207
6	148

* This sample size has caused detonation in confined molten AN at 230°C.

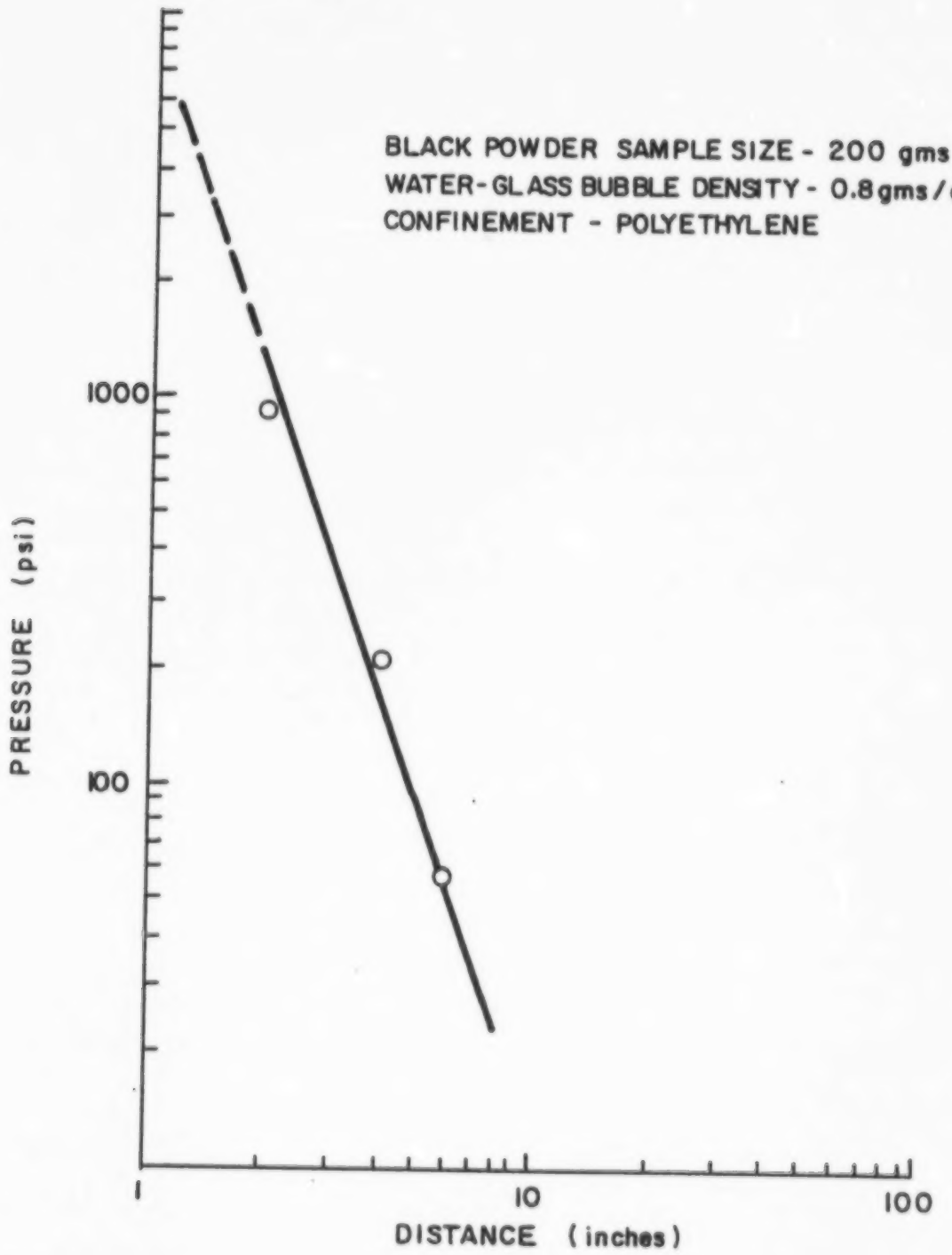


FIGURE 55 : PRESSURE – DISTANCE RELATIONS FOR 200 gm BLACK POWDER SAMPLES IGNITED IN WATER-GLASS BUBBLES AT $\rho_0 = 0.8$ gms/cm^3.

8. COOK-OFF TESTS

INTRODUCTION

Various deflagrating or pyrotechnic compositions based on ammonium nitrate, such as mixtures containing Al and carbon, Cu, Zn and other reactive metals were rapidly heated in small pyrex flasks, the experiments being described in earlier reports (29). Generally, the mixtures were very slow to burn at ambient temperatures when ignited on an open surface, but often reacted explosively when the mixture was melted, especially in the presence of Cu.

Under confinement in metal pipes, these mixtures reacted explosively when ignited, and, under certain conditions of confinement and geometry, this explosion was capable of detonating molten ammonium nitrate heated at 260°C.

4F Black Powder confined in metal pipes likewise initiated molten ammonium nitrate at 260°C.

4F Black Powder, contained in polyethylene bottles and ignited, was also capable of detonating molten ammonium nitrate at temperatures as low as 230°C.

A number of workers in the past (4) have observed that if a deflagration can be initiated in ammonium nitrate under conditions where the ambient pressure can increase as the reaction proceeds, the reaction transforms from a burning to a detonation at a pressure between several thousand psi for pure ammonium nitrate, and several hundred psi for fueled ammonium nitrate.

A reasonable explanation for this transition would be that an increase in pressure increases the equilibrium temperature for the reaction, hence the reaction rate. At some critical pressure level, the energy from the exothermic reaction is enough to overcome the moderating effect of the vapourization reaction, thereby resulting in a rapid

escalation of temperature and reaction rate which accelerates to detonation state conditions.

In order to study the effects of scaling up the previous small scale laboratory tests, several large scale heavily confined cook off tests with ammonium nitrate and powdered metals were conducted.

EXPERIMENTAL

Cookoff Cannister Construction

Steel cannisters for the tests were constructed of schedule 40 steel pipe and 1/4 inch steel plate. Cannister bodies were fabricated using 6 in. diameter pipe 33 1/2" long. Tops and bottoms were made from the steel plate and were welded into place. Two holes were drilled in the top plate with one in the centre serving as the exhaust orifice. This vent hole was threaded to admit couplings of various lengths to be employed as nozzles for the purpose of constricting material flow through the orifice. Hole sizes were varied from 1 in. to 1/2 in. The second hole was drilled and tapped on the cannister top to accommodate a thermocouple probe assembly.

In order to stand the cannister assembly over a propane burner, concrete blocks were used along with an angle iron grate. Figure 56 represents a completed cookoff cannister and stand arrangement.

Heat Source for Cookoff Cannister Tests

To provide the necessary heat required to boil large quantities of both liquid and solid explosive material, high pressure Sievert propane gas burners (No. 2942) having a heating rate of 57,000 BUT's/hour were employed as the heat source at a propane gas pressure of 15 psi. Electric squibs were used to ignite the burners remotely. The heating process was observed and recorded on video tape equipment set up inside a concrete bunker. Figure 57 is an illustration of the burner assembly used in the heat stability tests.

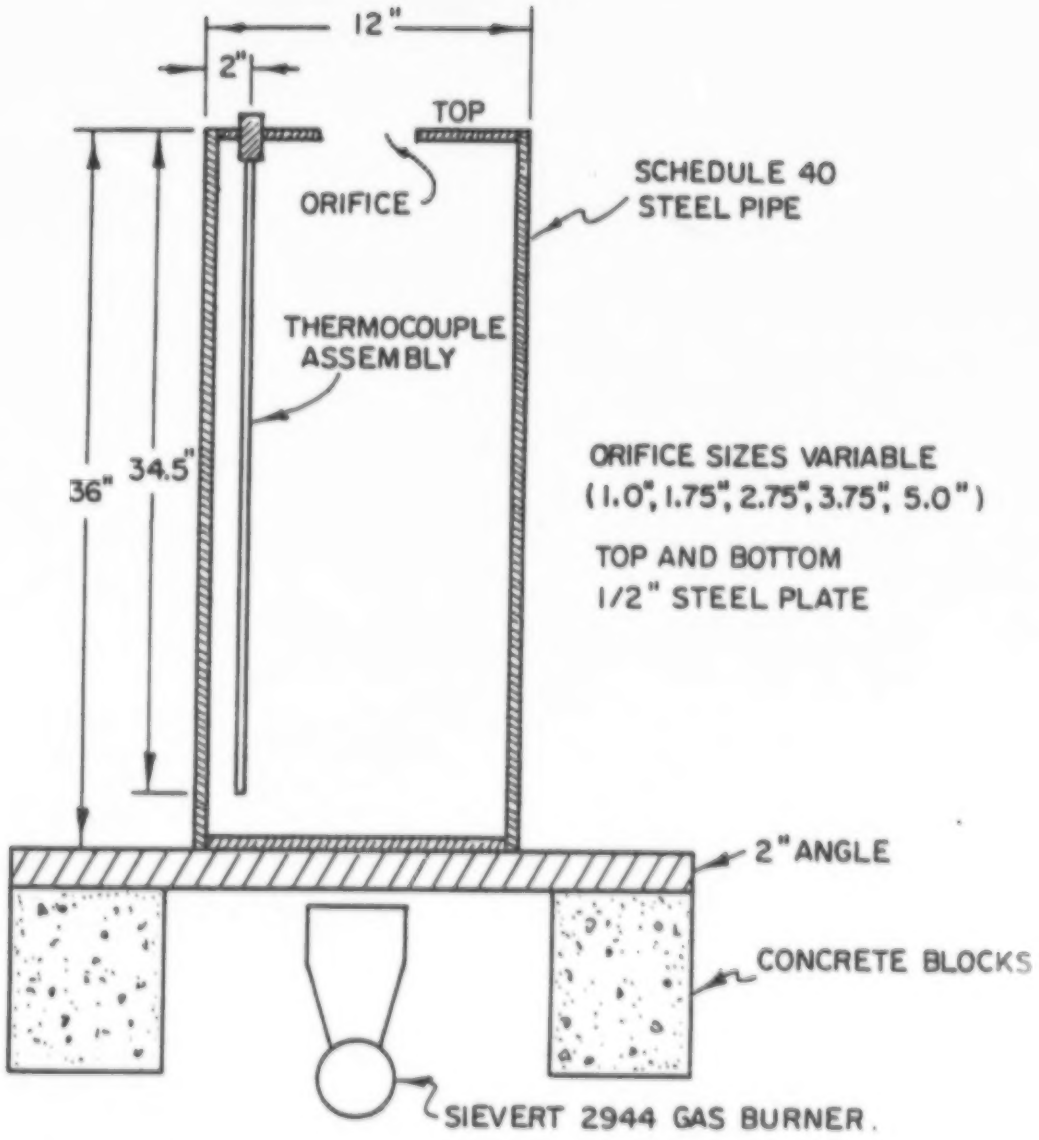


FIGURE 56: COOKOFF CANNISTER AND STAND ARRANGEMENT.

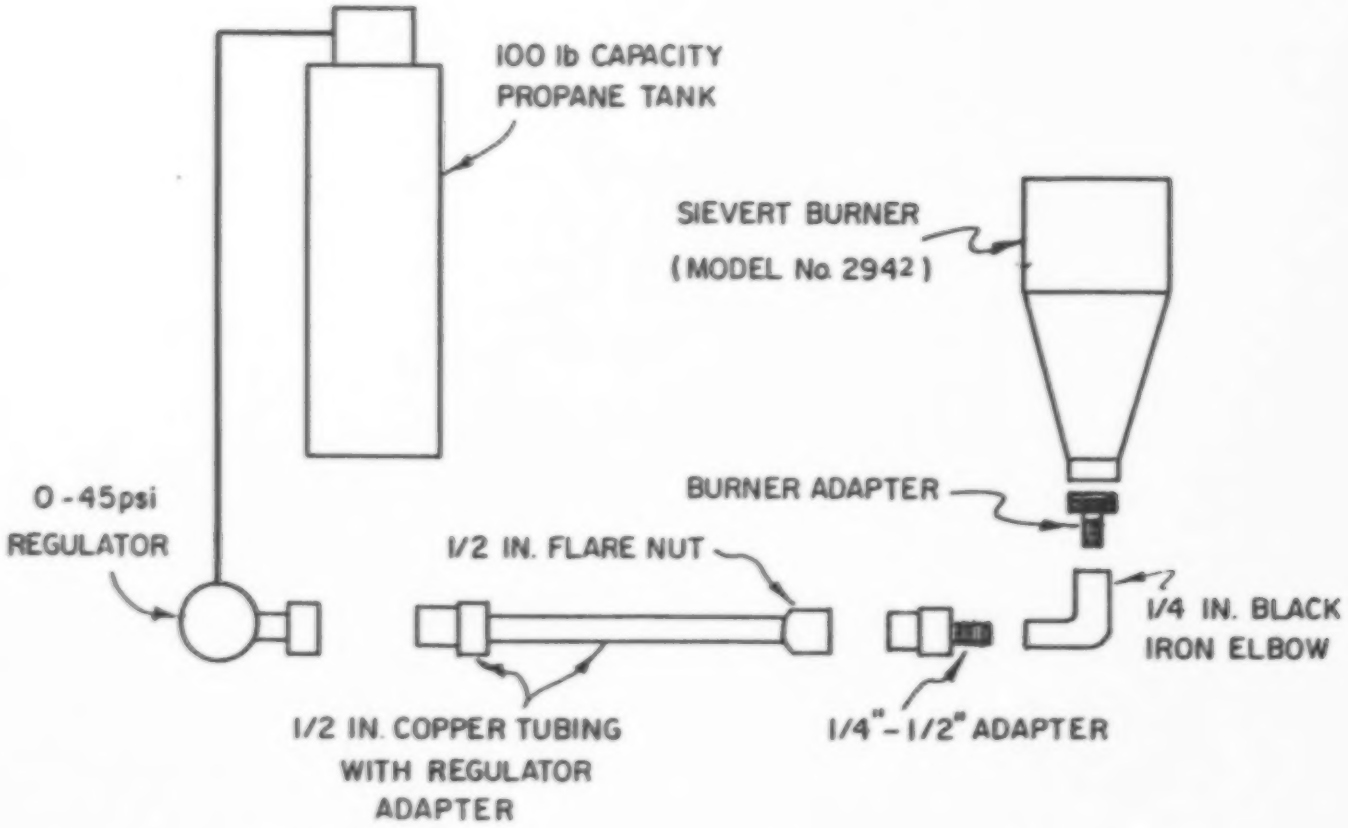


FIGURE 57: SIEVERT BURNER ASSEMBLY FOR USE WITH PROPANE GAS.

Instrumentation for Temperature and Pressure Monitoring in Cookoff Cannister

To determine the temperature of samples inside the cannister it was necessary to construct thermocouple probe assemblies which would measure temperature at the same point in all samples. High temperature thermocouple wire was used in conjunction with a millivolt chart recorder for recording temperature continuously.

Reactants

The cannisters were filled to the top with the following compositions:

1) AN/Ferric Oxide/Al with Fe_2O_3/Al used in a 3:1 ratio as a 5% mixture with powdered AN;

2) AN/Zinc 95/5

3) AN/Copper 95/5

4) AN/AL/Zinc 90/5/5.

RESULTS

AN/Ferric Oxide/Al

With the one inch vent, the product simply melted and boiled over, the molten residue solidifying on the outside of the container.

With the one half inch vent, the product vented brown fumes at a constant rate. There was no detonation or rupturing of the container.

AN/ZN

With the one inch vent, the product boiled over in a similar manner as did the AN/Fe_2O_3/Al mix.

With the one half inch vent, there was an initial rapid venting, followed by a rather sluggish decomposition, again with no violent effects.

AN/CU

With the one inch vent, the product vented off rapidly, venting forcefully towards the end.

With the one-half inch vent, the venting was violent and terminated in a detonation, rupturing the container and disintegrating the base plate.

AN/Al/Zn

With the one inch vent, the products vented off with no violent reaction. With the 1/2" vent, the products vented off violently, evolving brown fumes towards the end.

CONCLUSIONS

While the results were not unexpected on the basis of that of previous workers (4), the AN/Cu test did provide some unexpected results.

In the small lab scale tests, the AN/Cu mix generally underwent a rapid decomposition with the residue deflagrating somewhat like black powder, and evolving CuO, a similar reaction was observed. However, in the case of the one-half inch vent, the residue detonated.

In the presence of copper, formation of the tetrammine complex, $Cu(NH_3)_4(NO_3)_2$, is rapid when ammonium nitrate is in the molten state, and decomposes explosively on each occasion when it is strongly heated.

A study of the properties of "Tetramine Cupric Nitrate" was made by Picatinny Arsenal in 1943, (30), where it deemed necessary to obtain information on the degree of hazard involved in the use of copper or copper alloys in equipment used for the manufacture of amatol. It was found that "Tetramine Cupric Nitrate" has approximately the same impact senstitivity as lead azide. It also resembles lead azide with respect to brisance, as determined from sand test data. In the explosion temperature test, Tetramine Cupric Nitrate exploded in 5 seconds at 331°C, compared to 335°C for lead azide. Friction and Ballistic Mortar tests were conducted on "Tetramine Cupric Nitrate" by Dr. A king at the Canadian Explosives Research Laboratories (DEMR) near Ottawa in 1974. The friction test showed "Tetramine Cupric Nitrate" to lie somewhere between PETN and Perchlorate-Sulphur-Al mixtures in sensitivity. Ballistic Mortar tests showed that "Tetramine Cupric Nitrate", has 81% of the strength of TNT.

Clearly, the presence of (this metal complex) in a pool fire with molten ammonium nitrate represents a very hazardous situation.

Surface burning reactions or deflagrations, appear to

be ineffective in initiating a DDT in molten ammonium nitrate. If initiated over a large surface of several square feet, the results may be quite different. Similarly, if large amounts of molten metals were dropped into even large quantities of molten ammonium nitrate, a different sequence of events may be observed. However, in the quantities and geometry tested here, a DDT appears unlikely.

The deflagration of ammonium nitrate-Cu compositons may present serious hazards from the point of view of being able to readily detonate, given the extreme sensitivity (comparable to lead azide) of the Tetramine Cupric Nitrate complex. This complex has been shown to form readily with molten ammonium nitrate, and more testing should be done on its ability to initiate a detonation in molten ammonium nitrate. The presence of this compound may represent the biggest single hazard in pool fires involving contaminated ammonium nitrate.

Cupric nitrate also appears to be able to promote a rapid exothermic oxidation of metals such as Al which normally would not react too readily molten ammonium nitrate.

CONCLUSIONS

The shock sensitivity of ammonium nitrate, whether solid or liquid, is a strong function of density. Molten ammonium nitrate at 260°C has a bulk density of ≈ 0.8 grams/cm^3 and can be initiated to a stable detonation by a #6 Electric Blasting Cap. Prilled ammonium nitrate at the same bulk density cannot be successfully initiated with anything less than ≈ 100 grams of Pentolite. However, very fine grained or powdered ammonium nitrate with bulk densities of the order of 0.5 - 0.7 grams/cm^3 can be initiated with a #6 Electric Blasting Cap under strong confinement. Ammonium nitrate of this type can generally be produced by dissolving ammonium nitrate in liquid ammonia (anhydrous) and spraying the solution into a vacuum chamber to evaporate the ammonia, or by thermal cycling small quantities of crushed low density prills. This has been shown to be true by Fukuyama (29) in 1957. Bulk density is not the only factor which is important to the shock sensitivity of ammonium nitrate. The size of these "hot spots", air inclusions, microfracturing or substructure discontinuities, as well as their frequency of distribution are also factors.

Liquids are better shock transmitters than porous friable solids such as low density ammonium nitrate prills. However, the shock transmitting characteristics of an aerated boiling fluid differs considerably from that of the quiescent material, just as the shock transmission

characteristics of a large single crystal † of ammonium nitrate differs greatly from a large cylindrical tube of the same size filled with prilled ammonium nitrate.

The critical shock initiation parameters, i.e. shock pressure, shock velocity and particle velocity, have been determined for molten ammonium nitrate as a function of temperature, up to 260°C. At the higher temperatures the shock sensitivity of molten ammonium nitrate approaches that of a nitroglycerine based dynamite, which it also resembles when examined from the point of view of minimum primer weights. The shock sensitivity of the molten material, which is a strong function of bulk density, was not examined at temperatures much greater than 260°C because of the great difficulty in keeping the fluid in any vessel. The shock sensitivity may not, however, continue to increase at such a rapid rate, and may in fact begin to decrease as a result of the much lowered

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† Evans, in a paper titled "Detonation Sensitivity and Failure Diameter in Homogeneous Condensed Materials" (Evans, Marjorie W.: J. Chem. Phys. Volume 36, Number 1, 193 (1962) offered a theoretical treatment on the failure diameter of liquid TNT, and ammonium nitrate at theoretical crystalline density. In her treatment, a failure diameter of 6600 km was predicted for ammonium nitrate at the maximum theoretical crystalline density.

energy output in the detonation head. This trend has been witnessed with the solid material.

At temperatures much lower than 220°C the ability of the molten material to initiate and propagate a detonation is considerably reduced and at temperatures below 210°C is virtually non-detonable.

Between these two temperature extremes the sensitivity to shock shows an almost exponential increase.

The detonation characteristics of the molten material, i.e. velocity of detonation, critical diameter, velocity diameter curves, etc. reflect the density changes in the molten material as the temperature is varied from 220°C to 260°C. Detonation studies on the solid material and other explosives in general, show similar trends.

The shock initiation characteristics of the solid material, and in particular the prilled ammonium nitrate with bulk densities exceeding 0.9 grams/cm^3, reflect the importance of porosity, microfracturing and "hot spot formation" on detonation stability. An increase in density of 0.1 grams/cm^3 from 0.8 grams/cm^3 results in a very large and almost exponential decrease in shock sensitivity when examined from the point of view of critical or minimum primer requirements. This increase in density, however, is brought about at the exclusion of many of the pores normally present in a low density prill and consequently represents a very large decrease in the number of sites available for hot spot formation. In order to react enough prills in the detonation head to

provide sufficient energy for its propagation, the lack of available reactive sites must be accommodated by a larger detonation head. This requires a much larger primer to establish a stable detonation head.

Since this appears to be the case with the high density prills, the establishment of a stable detonation head would be quite sensitive to seemingly small changes in primer weights. A drop in primer weight from 98 lbs. of TNT to ≈67 lbs. of TNT almost resulted in detonation failure † with high density prills tested in the 8 ton series.

Future work should examine under what conditions a deflagration initiated in molten ammonium nitrate could cross over to a detonation, as this may be one, although unlikely mode of initiation under conditions of fire exposure. The deflagration to detonation transition (DDT) characteristics are not well understood for liquid explosives and little or nothing is known about the DDT characteristics of molten ammonium nitrate as a function of temperature. From a shock initiation standpoint the critical parameters have been determined. What remains is to determine how these can be set up by a deflagration.

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† Detonation failure in this case is understood to mean propagation failure, as evidenced by the curved (decaying) oscilloscope trace of a collapsing detonation probe.

Ammonium nitrate - water solutions or liquors are also transported and handled in tank car quantities on and off plants. The concentrations of these liquors generally average 83% to 85% but in Europe are frequently transported in tank car quantities at concentrations exceeding 95%. Taylor (31) has shown that ammonium nitrate liquors of this concentration are detonable.

A liquor of 95% concentration is frequently encountered in prilling operations.

The shock initiation and detonation characteristics of these liquors are not well understood. There is however, reason to expect, that their behavior is significantly different from that of the molten, anhydrous material when examined from the point of view of projectile impact, i.e. low amplitude shocks.

If "aeration" is a factor in shock sensitization for liquors, attention should be given to the effects of contaminantswhich can catalyze the thermal decomposition of ammonium nitrate at much lower temperatures than is normally required to thermally decompose the material. Transition metals and chlorides are known to do this.

Furthermore, in many ammonium nitrate manufacturing facilities, for example, urea "off gas" recovery of NH_3 is accomplished by bubbling the urea "off gas" through the liquor in the NH_3 - HNO_3 neutralizer. This has the effect of aerating or saturating the liquor with bubbles of NH_3 and CO_2 thereby effectively lowering the bulk density.

In situations such as this, the shock initiation characteristics of the liquor may be radically altered. It is this area which merits further investigation.

In this project the shock initiation characteristics of molten ammonium nitrate were altered by "aerating" the material via thermal decomposition products at elevated temperatures. It was shown with glass bubbles however, that aeration by thermal decomposition can be bypassed, and that the shock initiation characteristics of this mix do not differ significantly from that of the pure molten material at the same density. The significance of this is that if a pool of molten ammonium nitrate accumulates on an asphalt base, for example, and the molten ammonium nitrate begins to oxidize this material, the pool would be aerated with oxidation products and exhibit significantly different shock initiation characteristics than would be expected from such a pool which does not, on the surface, appear to be excessively hot. Under conditions of fire exposure, pool accumulation and contamination is not uncommon.

Thus the effects of contaminants in increasing or suppressing the shock sensitivity of either the molten or aqueous systems should be examined. The storage, transportation and handling of ammonium nitrate and ammonium nitrate liquors should then be reviewed in light of this data.

From the projectile impact (low amplitude shock initiation) tests, molten ammonium nitrate at temperatures greater than 230°C has been shown to be shock sensitive, and at temperatures of 260°C, is extremely shock sensitive, even in the unconfined state. Thus, the contamination of molten ammonium nitrate by copper can result in an extremely hazardous situation for three reasons:

i) it accelerates the decomposition of molten ammonium nitrate, thus serving to "aerate" the melt at temperatures much less than the normal decomposition temperature of 200-220°C;

ii) the residues of the reaction between copper and molten ammonium nitrate always contain the extremely sensitive tetramine salt, and its formation is rapid at high temperatures;

iii) the tetramine nitrate salt is very easily initiated.

Therefore, on the basis of the work conducted in this five year study, it can be stated that the presence of copper represents the single biggest hazard with respect to accidental detonation of ammonium nitrate under conditions of fire exposure.

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